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FISHING BOAT OFF LOFOTEN

With the Author's compliments.

# COD-LIVER OIL AND CHEMISTRY

BY

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## CHEMISTRY

THE LAW OF ATOMIC LINKING diagrammatically illustrated, pp. 1-508.

# PREFACE

When our firm was established by the late Peter Möller he laid down this principle —that those who use the commodity we prepare have a right to know all that we know concerning it. Since then a long period has elapsed, but that guiding principle of our founder has been constantly borne in mind ; and in order to carry it out we have from time to time published monographs on various matters relating to cod-liver oil.

These papers, however, do not seem to have attracted the attention that we venture to think they deserved, and in regard to the subject there still seems to be some amount of misconception, even in the best and latest text-books.

Hitherto our publications have been in a language that is perhaps not very accessible to English readers ; and as that may explain why the subject is not better known we have determined to issue this volume written in English, and dealing with all matters connected with cod-liver oil, and especially those likely to be of interest to members of the medical profession.

That, however, is but the reason in part. Our former papers have been published, not at indifferent times, but at the times when we happened to have something new to tell. This we now have in the results of the investigations lately undertaken by Mr. Heyerdahl. It is not too much to say that his discoveries make by far the most important contribution to our knowledge of cod-liver oil. In fact, they throw the first and only true light on that mystery, the real nature of the oil ; and to make this known is our second reason for issuing the present work.

In addition to the general information regarding cod-liver oil and the results of Mr. Heyerdahl's investigations we have utilised the opportunity to present certain other matters only indirectly connected with the subject proper. A more particular account of our reasons for introducing those extraneous matters will be found at the beginning of each section, and we hope that in some of them something of sufficient interest to be readable may be found.

The authorities for statements not derived from personal knowledge are too numerous to be specified in all cases, but here special reference must be made to the large amount of information derived from Captain JUEL's many able and interesting papers on Norwegian fisheries, published in *Norsk Fiskeritidende*; and to Mr. F. WALLEM's valuable official reports on fishery exhibitions in various countries; and, lastly, to the yearly statistical reports of the superintendents of the Lofoten fisheries.

43 SNOW HILL,
LONDON, E.C.

# NORWAY

## THE LAND OF THE MIDNIGHT SUN AND COD-LIVER OIL

In these days we are not all labelled exactly as we would wish. Poor Diogenes is 'a man who lived in a tub and did not wear any clothes to speak of'; and who knows or cares about his philosophic learning and doctrines? Rome is 'that big town where I bought these beautiful stockings,' and nothing more, to the young lady who has just 'done Europe.' Scotland is the land of 'cakes and kilts,' although it is said that there are canny Scots who could not tell a cake from a bannock, and who have never seen a kilt except as a somewhat embarrassing adornment to the English tourist. Were it possible to imagine anything so dreadful as a Scotchman parodying Burns he might well exclaim:—

> 'O wad some pow'r the giftie gie us,'
> *Tae lat folk ken hoo they should see us.*

As we do not seem to have acquired that 'giftie' yet, we must resign ourselves to our fate, and try to accept our fame from the wrong end: with thanks.

The fate of Norway is the midnight sun and cod-liver oil, but there are some other good things in the country, and the writer—himself 'made in Norway'—may be pardoned if he tries his little best to direct attention to them. A wider knowledge of these matters would certainly increase the sympathy and friendliness of the English people for their Norwegian cousins, and it is just possible that a more intimate acquaintance with the land where cod-liver oil is made, and with the people who make it, might increase even the present appreciation of that excellent article.

*The Country—General Physical Features.*—Norway is practically a vast mass of mountains stretching from the North Cape southwards for over a thousand miles to the Skager Rack—a great bulwark thrown up by Nature to shelter the low-lying countries around the Baltic from the Arctic and Atlantic storms. We have our doubts as to the inhabitants of these regions feeling properly grateful to their protectors, and even the Norwegian himself is at times tempted to think he could get on without quite so many hills. None the less he is proud of them, and justly, for they have a character and a charm that are all their own. Most of the great mountain ranges of the world can be taken only in graduated doses—the ascent of successive summits revealing higher and yet higher peaks beyond. In this way much of the effect is lost, but not so in Norway. There the mountains rise sheer up from sea to summit, and the combination of grey sea and sky, steep green slopes, dark frowning rocks, and snow-clad peaks forms a picture which is at once different from anything elsewhere, and is in itself impressive and sublime.

Whilst the mountains have decidedly the best of it in Norway, they have not succeeded in annexing quite everything, for here and there great rents break into the general mountain mass. These rents would be the valleys in other countries, but in Norway the ocean claims them as her own, forming the wonderful fjords—great waterways, nobler than the far-famed Rhine or Hudson, running from the sea to the centre of land, sending off branches now to this side, now to that, frequently closed in upon by the mountains jealous to say, 'Thus far shalt thou come, and no farther,' but again opening out and winding on under threatening cliffs, round snow-clad hills, past the thunder of waterfalls, past the grey gleam of glaciers, a bewildering, never-ending, ever-changing revelation of Nature in one of her wildest, grandest moods.

Norway is thus very much a 'land of the mountain and the flood,' and while these in their own way are no doubt excellent institutions, a nation cannot live by them alone. Unfortunately the other things seem to have been forgotten when Norway was being made. The area of land that can be cultivated is *less than one half per cent. of the whole*, or, to put the matter in another way, although Norway is larger than England, Scotland, and Ireland combined, its total arable land is barely equal to one of the smaller English counties. Nature, however, is always kind, and if she has been somewhat niggardly to Norway in the matter of land fit for the plough, she has given a compensation—the sea. Of this Norway has plenty. In fact the sea may be said to be 'laid on,' after the manner of gas or water, to almost every house in Norway. The vast coast line, which, including the fjords, may be put down at about 4,000 miles, brings the sea to every town and practically to every hamlet in the land, and the sea brings with it two blessings that make Norway what she is. One of those is the 'harvest of the deep'—a harvest of immense importance to Norway, and about which an account will be given in a later part of this book. The other blessing is of even greater moment; indeed, without it, the Norwegian would soon be as extinct as the dodo. It is in short the warmth that makes Norway a land where man may dwell. A more detailed account of this also will be given later, and all that need be said here is that nothing about Norway is more remarkable than that it should be a habitable country. Perhaps this may seem more striking if we remember that the country lies in the same latitudes and right opposite the perpetually ice-bound shores of Greenland, and that nearly half the coast of Norway is actually *within the Arctic Circle*.

*The People.*—If Norway as a country is thus unique, its inhabitants are not less so. There are in the orthodox fashion two distinct races, the aborigines and the invaders, and these are respectively the smallest and the tallest of European peoples. The Laplanders, the original *αὐτόχθονες*, can only succeed in reaching an average height of five feet and half an inch. According to the anthropologist they are brachycephalics—a most mortifying circumstance. Fortunately the Lapps are not likely to hear much about it; but if they should, they may calm their injured feelings by the comfortable assurance that things might have been worse. Indeed, fate might have placed them in Professor Sergi's hypsistenoclitobrachymetopusstenocratophicusneocaledonensic group, which we shall not further indicate, having no desire to bring this misfortune home to anybody. But to return to the Lapps, or Finns[1] as they are called in Norway. They are very few in number, and are now to be found chiefly in the extreme north of the country, where, for the most part, they live a nomadic life, subsisting on their herds of reindeer. They have all been converted to Christianity now, but they still retain a firm belief in devilry, exorcism, second-sight, and other inherited superstitions.

The Norwegians proper, the invaders, are a branch of the great Teutonic group of peoples.

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[1] Of course the Lapps have no connection with Finland or the Finlanders, who in Norway are known as Quanes.

There is nothing brachycephalic about them; they are a long-headed race, and long in another way, as they reach an average height of 5 feet 8½ inches. This is 'the record' for European nations; the next places being taken by the Scotch and the Swedes, whilst the English come in as a fairly respectable fourth with 5 feet 7 inches. It cannot, therefore, be said that the Norwegians are deficient in quantity—in quality, they are of course *sans reproche* in the opinion of the writer. Natural modesty keeps him from parading abroad the good qualities of his countrymen, but if anyone is in doubt about them, let him go to Norway and see the people as well as the scenery, and he will by no means return disappointed. In the formation of their national character, no doubt the Norwegians owe a great deal to their country. It is not exactly 'a land flowing with milk and honey,' but it is a land eminently fitted to cradle a brave, hardy, adventurous race, and this the Norwegians admittedly are. They are not a numerous people —at present numbering only about 2,000,000— but in shaping the destinies of Europe they have done more than many, if not, indeed, than any, of the far more numerous races.

*The Vikings.*—In olden times the Norwegians must have found the problem of existence no easy matter, and when they were forced to the conclusion that 'something had to be done,' it was pretty much a case of Hobson's choice. Hemmed in by the mountains on every hand but one, that one was their only course; they must 'go down to the sea in ships,' and they did, as not a few people came to know—to their cost.

The Vikings were not, however, the barbarian, bloodthirsty ruffians depicted by Anglo-Saxon and French chroniclers. For their time, indeed, they were a civilised and cultured race, with a wonderfully perfect legislation that will bear the brunt of criticism even in this present day. Warfare was the spirit of their age, and the Viking expeditions were the only school where young men of high birth might make a reputation by famous and heroic deeds. Their gods were gods of war, their heaven a place of fighting from the sunrise until the time for the feast in the great hall of Valhalla. Their hell was a place of cold and damp and darkness, the fate of cowards and of those who were unfortunate enough to die of old age or disease.

The Vikings are, therefore, hardly to be judged by the standards of the nineteenth century. Judged by the standards of their own age, they did that which was right in the eyes of men, and they did it well. Their adventurous voyages extended to almost every land of the known world. Their long, dark, low-hulled craft swept every coast, and whenever they could find a landing place it was *veni, vidi, vici.*

In Northern Europe, on the shores of Ilmen lake, the Viking Rurik laid the foundations of a state (A.D. 861), which has grown into the great Russian Empire. In Southern Europe they conquered Naples and Sicily (A.D. 1072). They were the foremost in the great conflict of the Cross against the Crescent, and for generations a company of Viking volunteers formed the body-guard of the Byzantine emperors. Towards the west they found their way as far as North America, a fact that until lately does not seem to have been known outside of Norway. Yet Leif Erikson looked upon the shores of the New World (A.D. 1000), nearly five hundred years before the famous Genoese discoverer was born, and not long afterwards a Viking, Thorfin, established a Norwegian settlement in New England, and there his wife Gudrid bore him a son, Snorre, the first 'native born American' of European blood. The inhabitants of the British Isles knew the Vikings well—and loved them little. Their frequent visits to Scotland have left many traces, both on the population and the language, and in Ireland they founded the towns of Dublin, Waterford, and Limerick. To the English people, however, the one episode of the Vikings is the story of Rollo and those who sailed with him on that memorable expedition which resulted in the conquest of the greater part of France, the formation of Norman chivalry, the destruction of the Saxon power at Hastings, and therefrom the development of the England of to-day.

This Rollo or Rolf, surnamed the Ganger (the walker), because no horse could be found high enough to lift him off his feet, was condemned to exile by the king, Harold Fairhair. He went, but not alone, for he was the hero of the 'Young Norwegian,' and what were kingly smiles to be weighed against the wild adventures of a foray when 'the Ganger' led the way! And so they sailed, as their fathers had done before them, a reckless band caring not what lay in front, ready for anything the gods might bring; but little dreaming that in their hands they held the fate of nations, that their foray was to change the history of the world. It may interest some English people to know that the home of Rollo's childhood still exists. He was the son of Ragnvald Mörejarl (the Earl of Möre), and visitors to Söndmöre (South Möre) who care to make a pilgrimage to the island Vigra will there find Roald (Rolf's hall), and near it the ancient shipyard, whence doubtless many a Viking craft was launched. In the neighbourhood, also, are several other ancient remains connected by tradition with Rollo and his Viking ancestors.

*The Fall of Norway.*—The Viking age was no doubt the golden age of Norway, but it meant a serious drain upon the Norwegians. The best and bravest were ever sailing away over the Northern Ocean—and they seldom returned. The sea claimed them, or the battle, or they found their homes and their work in other lands as leaders of men, as moulders of the nations that were rising from the chaos of the middle ages. The signs of this drain of strength were not, it is true, very markedly shown, and the Norwegians who remained at home might have held their own against all comers had it not been for the intervention of a more terrible invader—the pestilence of 1349.

In these present days we have our epidemics and other outbreaks of disease, and though they are bad enough, they do not enable us to form even a vague idea of the calamity that now overtook the Norwegian people. The shadow of the dark wings rested on every town and village and homestead in the land. None were spared—gentle and simple, rich and poor, youth, manhood, and old age, shared alike and equally the common fate. Everywhere was the sound of mourning, save where, in silence, only the dead were left to bury the dead. In many parishes and valleys not a single soul survived, and, when at length the hand of the destroyer was stayed, barely a third of the population remained alive.

This appalling disaster was a fatal blow to Norway's power, and also to her independence. Never thickly peopled, the country was now little better than a desert, and its few remaining inhabitants were paralysed by the calamity and scattered over a wide region unfavourable for defensive combination but everywhere open to attack. Her enterprising neighbours were only too ready to take advantage of Norway's helpless condition, and she was soon turned into a kind of 'sphere of interest' for the advantage chiefly of the Hanseatic towns. But even yet the cup of Norway's miseries was not full. Her crown passed by inheritance to the Danish kings, but they, not content with such a peaceful union, eventually turned it into possession by right of conquest, and now indeed the glory had departed. Norway was a mere province of Denmark, and in this state of degradation she remained until the beginning of the present century.

At the end of the Napoleonic wars Denmark found herself on the losing side, and the triumphant allied powers decreed for her punishment that she should hand over Norway to the Swedish king. This was no doubt a most convenient arrangement—from the Swedish point of view. The Norwegians, however, felt that they also had some little interest in the matter, and, calmly ignoring the allied powers, they determined to settle their own affairs to suit themselves. They had had quite enough of playing the part of a province, and they declared Norway once again a free and independent land. They knew that they were now too strong to be coerced by either Sweden or Denmark, and they knew the decree was not likely to be forced upon them by the allied powers, who were far too much in love with the peace they had just obtained to think of risking it for anything of the kind. The Norwegians were perfectly successful in carrying their point, and they then entered into a defensive union with Sweden, nothing being in common except the crown and the ambassadorial and consular representation.

This union has not, however, been altogether a success. The Norwegians considered it a partnership on equal terms, and naturally expected a partner's share in the control of foreign matters. The Swedes, on the other hand, did not quite see this view, and they showed so little haste in making the necessary re-arrangements of their Foreign Office that—it is not done unto this day. Thus the share obtained by Norway was merely nominal, and thus also the little 'rift in the lute' appeared, and, after the manner of its kind, it grew until in 1885 the erstwhile happy union seemed perilously near divorce proceedings. The crowning cause of offence at this time was a change in the organisation of the Foreign Office by which even the nominal influence that Norway had so far enjoyed was reformed out of existence. The Swedes did not seem to think it necessary that their consort should be a consenting party to this arrangement, but for once their high-handed proceedings had gone too far. In Norway universal indignation prevailed. The moderate counsel of the conservative party was to try the influence of sweet reasonableness once again, but the radical party, who had a small majority in the *Storthing*, proposed that Norway should do as she was done by, and manage her foreign affairs for herself. The King then used his suspensive veto to the best of his ability. He repeatedly changed his ministry from radical to conservative, and *vice versâ*, and is at the present moment (1894) governing the country with a conservative ministry in the face of a radical majority in the *Storthing*. The Swedes rather tardily recognised the mistake they had made in 1885, but, being the larger of the two nations, they will not listen to the claim of equality; which is, perhaps, natural enough from their point of view; and thus the quarrel still drags its weary way. At present the matter seems to be again approaching a crisis—indeed, it has become so acute that it may be heard of even outside Norway, and frequent references to it appear in English newspapers, generally under the astonishing title, 'Home Rule in Norway'!

*The Norwegian of To-day.*—It is a far cry from the *Berserks*, who followed Rolf or Regnar Lodbrok, to the present-day Norwegian, but he nevertheless is the direct descendant of the Vikings. In his veins flows that very blood which is the boast of aristocracy, and which, the genealogists tell us, runs from Harold Fairhair (936) through every royal line of Europe, those of Turkey and Montenegro alone excepted. In England nowadays very few of the nobility and gentry can go back to the sacred Roll of Battle Abbey and the unkind person might call their claims to Viking blood just a little bit shady. Certainly if they do have it, it is in very 'dilute solution,' but none the less most highly prized. The old Norman families, however, such as the ducal houses of Norfolk, Leinster, and Northumberland, the noblest of the noble, the proudest of the proud, are blood relations to the Norwegians, to simple folk—mayhap deck hands on trading skiffs, or poor cod-fishers off Lofoten.

With all these high and noble connections we would naturally expect the Norwegian to be a most aristocratic personage, and so he is, to his very finger tips, in many ways. He is no despiser of pedigrees, and men in every station of life are to be found, including nearly all the udal farmers, who can trace their ancestry farther back than most of the nobility of other lands, many of them indeed being able to prove direct descent from the old Norse kings. But despite all this the Norwegian is very much the democrat. The Saga relates of Rollo the Ganger and his men that when they landed in France one of them was asked, 'Who is your master?' and he replied, 'We have no master, we be all equals.' Even the long series of misfortunes through which the Norwegians have since passed has not stamped out that strong sense of self-esteem. They hold that 'all men are equal,' and in Norway, no matter what his fortune or his forefathers, 'a man's a man for a' that.'

The result of this curious mixture of the aristocrat and the democrat is sometimes almost comic. The Norwegian will acknowledge no man as his superior—openly: but his soul longs for distinction *honoris causa.* Were the old sea-kings to come to life again he would throw prudence and everything else to the winds and sail away with them to foray and fight, and die for that vanity of vanities—empty glory. As it is, however, he has to content himself with things much more prosaic. Nowadays he descends upon the coast of France or England in the unromantic form of a Cook's tourist, and at home there is but one 'distinction' to which he can aspire, 'the most sacred order of St. Olaf.' That such an order should be tolerated by a people professedly democratic, nay even republican, is in itself, of course, an anomaly, but it is still more surprising to see the radical party, when out of office, fervently urging its abolition in the interests of the public weal, and, as soon as they succeed in seizing the reins of government, hastening to deck themselves with its despised, yet comforting insignia. But perhaps the climax is reached when we see two of Norway's poets, writers of world-wide reputation, taking from each other a solemn vow never to accept a royal favour of this disparaged kind, and then, in the daily press, disputing as to who had broken the pledge—first.

Despite these little vanities, however, the Norwegians on the whole are not a bad lot. They have the right stuff in them, and all the natural surroundings to bring it out—the two essentials for the making of a nation great in the true sense of the word. That they have the right stuff in them none who have studied in history the doings of the Norwegians will deny. That their surroundings have called forth their capabilities is no less obvious. Ever since the great pestilence they have had a struggle with man—a long and an uphill fight with all the odds against them, but in the end they justified themselves by success. With nature they have had and still have a daily battle for bare existence, and here also the struggle that brings immediate success brings something more—strength for future and higher and better things.

This is not mere idle speculation, and now that Norway is herself again, a free nation with all the stimulus that comes of freedom, she is beginning to show the world that she can do something in the 'higher paths of life.' Of course she must be judged by her fruits, but those who cannot judge without the thing odious—comparison—should bear in mind that the Norwegians number less than two millions, less than half the population of Lancashire, little more than a third the population of London. They cannot therefore be compared with a first-class nation. The doctrine of averages is strongly against the occurrence of master minds in small communities, and it is only with such nations as her near neighbours, Sweden and Denmark, that Norway can be fairly entered. If this be done she will not fare badly, with such representatives as the composers Grieg and Johan Svendsen, the musicians Oluf Svendsen and Ole Bull, the three brothers Sinding, painter, sculptor, and composer, the politician-poet Björnson, and the problem provider Henrik Ibsen. After all, however, such matters as literature and art are of far less importance in the life of a nation than 'the greatest good of the greatest number.' This inevitably leads us into Norwegian sociology—a subject too vast to be treated here, although a few of its aspects which may have some special interest to English readers will be mentioned.

*The Temperance Question in Norway.*—It may be said safely that the Norwegians are *the temperate people* of Europe; the people to delight the heart of the teetotal orator, unless, indeed, he be in search of employment. They were not always, however, such a bright and shining example; in fact, not long ago they were very much the reverse. Their alcoholic heredity was of fairly respectable date, for the Vikings understood the value of 'the cup that cheers.' Their descendants, also, understood it, and so well that in 1838 the temperance question became perforce the question of the day. An attempt was made to limit the production of alcohol by imposing a duty of 1*s.* 4*d.* per gallon, and this was gradually increased to the present rate of 7*s.* per gallon, of absolute alcohol. Also the use of stills of less than fifty gallons capacity was prohibited. Some idea of the need for this prohibition, and of the drinking powers of the Norweigan, may be gained from the fact that in 1838 there were no less than 9,727 stills in use, or, in other words, every 120 Norwegians were the happy owners of a still producing spirits for their special benefit.

These, however, were only the opening skirmishes of the battle against King Alcohol, and they were followed up until that individual fell from his high estate to one most humble and obscure. At present the Gothenburg system is established in every town in Norway. This means that practically the whole of the retail business of each town is concentrated into the hands of a single company, which is allowed to retain a fixed *low percentage* of the profits, but is obliged to distribute everything over and above amongst charitable institutions. In Christiania, which may be taken as an example, there is a population of 160,000, and only twenty-seven places are authorised by the company to retail liquor. These are rendered as unattractive as possible, and, as if ashamed of their calling, they hide themselves away behind their more respectable neighbours. A small enamelled plate upon the door is the only indication that refreshments may be had within. The glowing lights and mirrors and show-cards of the English gin-palace are chiefly conspicuous by absence, and, instead, the dismal light shows walls decked with scriptural texts, setting forth a solemn warning against the 'evil spirit.' There is no 'saloon bar,' no snug corner, not even a seat. No alluring siren stands behind the counter, but a 'ministering angel,' of the mature variety, glances over her spectacles with a look of kindly welcome duly tempered by reproof, and whilst reluctantly purveying the drinks, she never fails to recommend that crowning enormity of modern civilisation—sandwiches. She is allowed a small percentage on the sale of these, no doubt with deep intent upon the preservation of the species whose habitat is her domain.

The country districts, unlike the towns, take their temperance in the form of local option, and find it satisfactory. It is different, however, with the unwary stranger who does not find local option very refreshing, and has even been known to say uncharitable things strongly when he discovers that his favourite tipple can be had—fifty or a hundred miles away. It is no joke to have to send, perhaps, as far as from London to Birmingham for the 'something' to mix with your soda, and to those who cannot visit Norway without this 'adjuvant,' our advice would be—take the 'active principle' with you.

In other respects temperance legislation seems to have scored a success in Norway. The 9,727 stills have been reduced to twenty-four. The yearly consumption of spirits, calculated as absolute alcohol, has been reduced to three pints per head of population. Drunkenness is practically unknown; and to the younger generation in the country districts, the sight of one who has indulged, 'not wisely, but too well,' would be an absolutely new experience. This, however, is not all, for we are told that the sins of the toper are visited upon his children in the form of a high infantile mortality, epilepsy, idiotcy, and insanity, and the statistical records of Norway[1] show that these undesirable legacies have been a diminishing quantity ever since temperance came into possession.

*Land in Norway.*—The land question in Norway by no means holds the field as it does in certain other countries we might mention. Nevertheless it is a very interesting question, not only to those immediately concerned, but to every student of sociology. The Norwegian is essentially conservative in his nature, doing as did his forefathers; and as a consequence his system of land tenure is a survival from the earliest Teutonic times. In its main features indeed the system does not differ materially from that seen and described by the Roman historian Tacitus, nearly 2,000 years ago.

The farms in Norway are held on a freehold right regulated by two laws of very ancient origin—the *Aasædesretten* (homestead law) and the *Odelsretten* (udal law). The former regulates the inheritance of the freehold which passes from the father to his eldest son, or to the eldest daughter, should there be no sons. If there are several children the value of the estate is divided into equal shares, and the eldest son has to pay such shares to each of his brothers and sisters before he himself can enter into possession. The arrangement seems rather hard on the eldest son, and would sometimes really be so were it not that his burden can be lightened by the father, who, with certain limitations, has the power of fixing the value of the estate at what he thinks proper, and the children must abide by his decision.

The other law, the *Odelsretten*, secures the freehold to the family. The holder of the farm can offer it for sale, but the members of the family have certain privileges over outsiders in purchasing it. Further, should it be sold to an outsider any member of the family can redeem it within five years by paying the original price together with compensation for any improvements that may have been carried out. This udal right has often been vigorously assailed. It is said to be injurious to the interests of agriculture, because the purchaser of a farm is not likely to undertake extensive improvements when he knows that he may be compelled to sell it at a moment's notice. On the other hand, and especially by those in possession, it is said to be a most excellent law, as it protects the genuine farmer from the rich townspeople, with their propensities for buying land and forming large estates.

Whatever may be the theoretical right or wrong of the system, there is no denying that in practice it works tolerably well. Norway is hardly a land of smiling skies and pregnant soil, and its area is scarcely 800 square miles—from the agricultural point of view. Yet, on this mere patch of land, with some rough hill pasture thrown in, no less than one million people contrive to exist, and to hold their heads up fairly well.

The udal system has also preserved for us a beautiful picture of life as it was in the days of our remote forefathers. Each Norwegian farm is the home of a little community, complete in itself, and strongly bound together by ties of common interest. The head of this community is the freeholder, the *Gaardmand*, and the house where he and his family dwell is *the homestead*, which is surrounded by a number of other families each with a little piece of land and a house of its own. The head of each of these families is known as a *Husmand*, and in return for his *Husmandsplads* he assists in the general working of the farm, as a rule giving a certain fixed number of days to this yearly.

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[1] The mortality of infants under one year of age has been reduced to 10·86 per cent., as against 15·48 per cent. in England, 17·35 per cent. in Belgium, 21·96 per cent. in Prussia, 25·82 per cent. in Austria, and 32·36 per cent. in Bavaria. This low infantile mortality is the main factor of the rapid increase of the Norwegian population, which shows a higher ratio at present than any other European race, although the birth-rate is rather under the average.

The effect of the temperance movement upon the proportion of epileptic and idiotic children was specially investigated by the late Dr. Dahl, director-in-chief of the Government Medical Department. He visited the greater part of the valleys in Norway, first in 1855 and again in 1865, for the express purpose of personally investigating the matter; and he found that this unfortunate class of children had decreased by 16 per cent. during the ten years, although during the same period the population had increased by 14 per cent.

In regard to insanity, in 1860 13 per cent. of the inmates of lunatic asylums were habitual drunkards; in 1870 the proportion was 7 per cent.; in 1880 3 per cent.; and in 1890 only 2½ per cent. The number of suicides has decreased from 109 per million annually in 1846–50, to 67 annually in 1881–85, whilst in other countries the number has been increasing: in England reaching 85, in Sweden 95, and in Denmark 275. Crimes directly connected with drink have also decreased in a remarkable degree, and murder is now so rare as to be practically unknown.

The *Gaardmand* is generally the possessor of 'a lang pedigree' extending back in some cases for nearly a thousand years, and in his own way he is as proud of this as if it were a coronet decked with the significant strawberry leaves. He would look upon a marriage between a member of his family and a member of a *Husmand's* family as a terrible *mésalliance*, just as the most aristocratic families in England do in circumstances similar, yet somewhat different.

But although the *Gaardmand* stands very much on his dignity in some ways, in others he has no dignity at all. He makes no difference in his daily life from that of those around him. He and his labourers meet and speak, not as master and servant, but as men and equals. They dress alike and they labour alike, and when the day's work is over they sit down at a common table and fare alike, the *Gaardmand* presiding at the head of the board in the true patriarchal style.

*Norwegian Shipping.*—The Norwegians are eminently a seafaring race, and they are so simply on account of what the scientist would call their 'environment.' Every tendency, hereditary and acquired, impels the young Norwegian to go to sea. He comes of a stock that has done so from the remotest ages, and certainly the heredity ought to be well grained in. He himself has the sea and its sights ever before his eyes from the first day that he opens them, and the stories that tickle his youthful ears are tales of the sea, of the heroes of the Viking age, of the daring deeds and hairbreadth escapes of the present day, and these, mayhap, fresh from the lips of those who have seen or done them.

When to all this we add that there is little to tempt the young Norwegian to stay at home, it will not seem surprising that he takes to the sea very much as a duckling to its pond. The merest child in Norway knows how to handle a boat, and perhaps nothing more astonishes a stranger on his first visit to the country than when his ship happens to meet one of the pilot-boats cruising far out from the coast, and he sees the pilot step on board, calmly leaving behind him a boy, *not yet in his teens*, to find his way home as best he may, 'wind and weather notwithstanding.' With this sort of training the Norwegians ought to become good sailors; that they do so, can be testified by the English yachtsmen who have matched themselves against the smart seamanship of the Norwegians sailing under the pennant of the New York Y.C.

The truth of the Sagas, relating how the Norsemen crossed the Atlantic in their open boats, has on more occasions than one been challenged, but in 1893 it was shown that the feat was only child's play to Norwegian sailors. A crew of them made their way from Norway to Chicago in an exact model of the ancient Viking ship that was dug up at Gokstad some years ago. The model was 70 feet in length, undecked, and fitted with a single mast and square sail. Her sides were pierced for oars, some 16 feet and others 19 feet long, and she was manned by a crew of twelve sailors, one of whom humorously remarked to us just before starting, 'The only thing about which we may quarrel is as to who shall secure the 16-foot oars.'

The boat in which Leif Erikson crossed the Atlantic was probably much larger than the Gokstad boat, for we know that some of the Viking ships carried between two and three hundred men, and one of the Sagas tells us that the 'Long Serpent,' built by the celebrated shipbuilder Thorberg, was 140 feet in length. The feat of last year, therefore, proved that the tale of the Sagas was far from being impossible; and another thing also was proved—that the daring spirit of the old Vikings is not altogether dead in the Norwegians of to-day. If further proof be wanted it may be seen in Captain Jörgensen and his mate Nilsen's astonishing voyage, all the way from England to Australia, in the 'Storm King,' a boat 30 ft. long; in Adolph Fritsch's recent adventurous journey single-handed across the Atlantic in the 'Nina,' 40 ft. long; or in Dr. Nansen's expedition, now trying to reach the North Pole; or the Wellman Polar Expedition, half of whose members hail from Norway.

Polar expeditions and the like are, however, only for the few, and the great bulk of Norwegian seamen content themselves with the much more prosaic mercantile service. In regard to this, Norway occupies a most remarkable position. She is only a small country; her population is less than two millions; and yet she owns a fleet that occupies the third place[1] amongst the navies of the world, being surpassed only by those of England and the United States. But relative to her size, Norway is easily first of all seafaring nations; for every thousand Norwegians own 792 tons of shipping, while the English, who come next, have only 322 tons for each thousand individuals.

The mercantile navy of Norway is not the property of a few wealthy capitalists or companies, as is the case in some countries, but it is the people's own, and in it a great part of their savings is invested. There are few Norwegian families without a pecuniary interest in some ship or ships, or without some relatives on board them; and in this way the shipping has become in Norway, more than anywhere else, a national institution in which everyone is in one way or other directly interested.

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[1] England, 11,597,106 tons; United States, 1,823,882 tons; Norway, 1,589,355 tons (*Naut. Mag.*, September 1890).

## THE NORWEGIAN FISHERIES

In most countries the fisheries and the fishermen occupy a very secondary position in the industrial and social scale, but in Norway it has always been quite the reverse. The mythologies of Egypt, Greece, and Rome had special gods in plenty, but none to spare for those who reap the harvest of the sea. With the old Norse gods it was a different story—Ægir and his consort Ran were the special guardians of the fisher-folk, and seven daughters, blue-eyed and golden-haired, aided their gracious task. Even Thor, the mighty god of thunder and of storm, did not disdain the gentle art, and we read that once, with Hymer, he went fishing. Surely never before nor since did such an angler cast a line, and those who know and love the dun-fly and the spider-black might well adopt him as the angler's god—old Izaak notwithstanding.

In our own *fin-de-siècle* age Thor and his fellow deities are a little at a discount, but none the less their story has a meaning to the philosophic mind. The gods alike of Egypt, Greece, and Norway were but the reflection of the lives and aspirations of the people, and through them we may read the tale of how the people lived and thought. This special instance throws a light upon the fisheries of Norway in pre-Christian times, and shows how largely they then bulked in the everyday life and estimation of the Norwegian people.

In the middle ages our knowledge of the Norwegian fisheries becomes something more than a mere deduction from mythology. Historical records deal with the matter, giving us a definite idea of the details and importance of the industry, and showing how fitting a school it was for an adventurous sea-faring race, and how the distinguished men and families of these times had all of them their origin in just those regions where the richest fisheries take place.

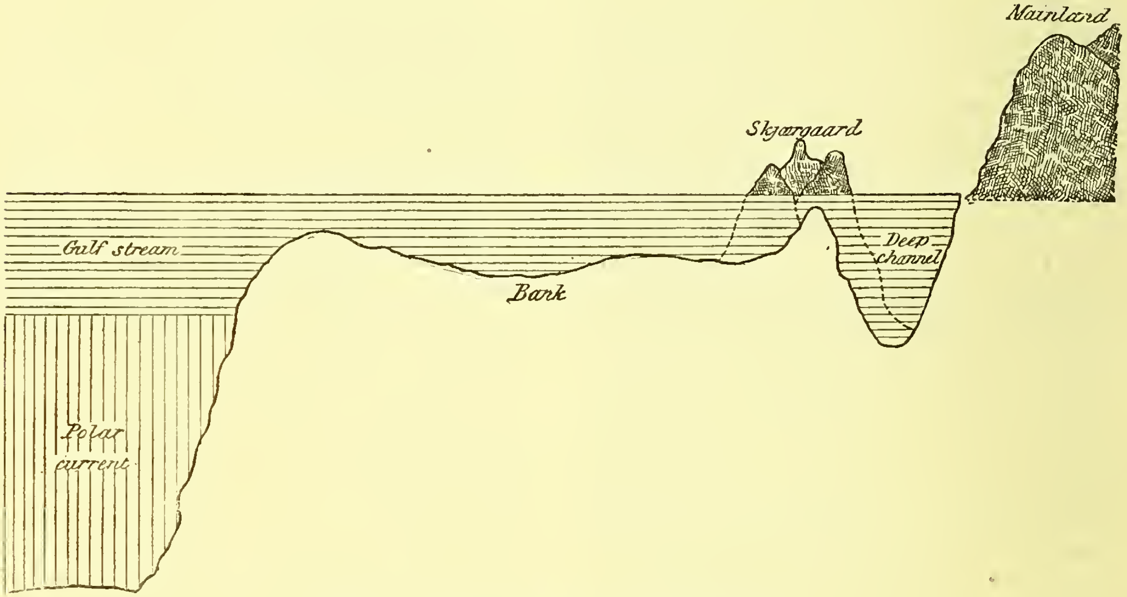
### THE NORWEGIAN SEABOARD.

We may gather from these records that the Norwegian fisheries were of very considerable value in days gone by, and they are certainly no less so in the present day. The reason for all this is to be found in the conformation of the Norwegian coast, which holds out attractions of a 'highly desirable' nature to the fish and to the fishermen who catch them.

The Scandinavian peninsula may be described as a great slope, beginning at the low-lying coasts of Sweden on the Baltic Sea and the Gulf of Bothnia, gradually rising towards the west, culminating in the great mountain-chain of Norway, and then suddenly falling sheer into the waters of the Arctic and Atlantic Oceans. This sudden fall is a point of no little importance. It does not stop at sea-level, but continues downward, so that even close to the shore the soundings are frequently of immense depth, forming a deep channel which in former times must have extended along, practically, the whole length of the Norwegian coast from the North Cape to the Naze, but is now, at frequent intervals, partly filled with disintegrations brought down in past ages from the mountains by glaciers and rivers. This deep channel also runs into the fjords, even the longest of them, such as Hardangerfjord, 70 miles in length, Trondhjemsfjord, 90 miles, and Sognefjord, 100 miles; and in depth nearly 700 fathoms.

From the outer side of the deep channel, and running parallel to the shore, there rises a secondary mountain range. The higher summits of this range emerge from the sea, sometimes to the very respectable height of two or three thousand feet, and in this way they form an almost continuous chain of islands—the *Skjærgaard* — extending along the whole length of the Norwegian coast. The deep channel between these islands and the mainland is called the 'inner passage,' and to this the *Skjærgaard* acts like a great breakwater: outside the storms may rage after the most approved North Atlantic fashion, but within the sheltering isles the waters of the inner passage lie calm and undisturbed.

To the outer side of the secondary mountain range the sea bed rises into a high bank or plateau. This plateau, like the string of islands, follows the general contour of the mainland. It is of somewhat variable width, and only from 50 to 200 fathoms below the surface. At its outer or seaward side it suddenly terminates in an enormous precipice, which at some places takes a plunge right down for about 8,000 feet to the deep bed of the Atlantic.



PROFILE OF THE SEA-BED OFF THE NORWEGIAN COAST.

This plateau with its great wall-like western face might be described as Norway's guardian angel, holding the ocean currents in watch and ward on her behalf. It allows the warm waters of the Gulf Stream to pass, and crossing the plateau they pour into and fill the inner passage. On the other hand it keeps back the cold waters of the Arctic currents, which flow at a lower level in the ocean than the Gulf Stream, and, striking against the face of the plateau, are turned away again into the deep Atlantic bed. This formation of the Norwegian coast is represented by the accompanying diagram.

If we regard the seaboard of Norway simply as an apparatus devised for the benefit of the climate, then it would be difficult to imagine anything better adapted for the end in view. Iced water may be a very excellent thing in its own place, but in Norway the only place for it is the bottom of the Atlantic—where it is. Warmth, again, is the one thing needful, and the genial stream that brings it is not only admitted passage free, but is provided with 'suitable accommodation,' where it may rest after its long journey from the Spanish Main. It is no ungrateful guest, and its kindly payment to its host is life, and all that life implies.

Here, also, we see the *raison d'être* for the extraordinary coast line of Norway. It has been constructed so that each and every part of the country shall share in the benefits of the 'hot-water supply' that is, in the waters of the deep channel, and the arrangement of countless isles, and a mainland broken up by equally countless fjords provides that few districts in Norway are left out in the cold. In an earlier part of this work it was stated that nothing about Norway is more remarkable than that it should be a habitable land, but how much more remarkable is it if we consider the means by which it is brought about! The outer wall, the plateau, the island chain, the deep passage, the fjords—each playing its own part, each part essential to the whole, and the whole a combination exceedingly efficient for its purpose, and wonderfully striking as an illustration of Nature's ways.

### THE COD FISHERIES.

The above conditions are not only good for man—they are also good for fish. Despite the high latitudes, the waters off the Norwegian coast are never frozen, even in the severest winters, and fish of many different species live and thrive in them most amazingly. The chief varieties are the herring, mackerel, ling, coal-fish, and last but by no means least, vast shoals of cod.[1]

The cod fisheries are of two kinds—the permanent and the periodic. The permanent fishery goes on all the year round in the waters immediately adjacent to the coast. It supplies the daily demands in various localities, and although there are no statistics enabling us to show exactly its importance, still the aggregate take must be considerable. Compared, however, with the periodic fisheries, it sinks into insignificance, and from it there is no production of cod-liver oil worth mentioning.

The periodic fishery is of two kinds: the *Gydefiske*, spawning fishery, and the *Loddefiske* or Finmark[1] fishery. These entirely differ in regard to the locality where the fish are caught, the season at which they are caught, and the reason why they come there to be caught.

The *Gydefiske* takes place in the winter season all along the coast of Norway, but especially at two localities: off the entrance to Moldefjord, lat. 62° to 63°, and at Lofoten, lat. 68°.

Immense shoals of cod-fish resort to these localities for spawning purposes. They appear on the fishing grounds early in January, in March they spawn, and in April they are 'gone, leaving no address.' Their exact habitat is somewhat of a mystery. Unlike the cod-fish of the permanent fishery, they do not live in the deep channel close to the land, and probably their home is on the outer plateau, especially near that part where the great wall descends to the bed of the Arctic and Atlantic Oceans. Why they come to these particular localities to spawn is another mystery. Scientists assert that it is because there the young fry find sheltered places where they can safely grow and thrive. Of course, the scientists must be right; but it is rather curious that some cod-fish manage to get on well enough without making the Norwegian or any other coast their nursery.

Another theory puts the blame on a kindly Providence which acts somewhat after the manner of the Society for the Prevention of Cruelty to Children. It sends the cod-fish

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[1] The following table shows the relative importance of the various fisheries:—

| | |
|---|---|
| Cod-fish . . . . . | 61 per cent. |
| Herring . . . . . | 25 „ |
| Coal-fish and ling . . . | 8 „ |
| Mackerel . . . . . | 3 „ |
| Salmon and sea-trout . . | 2 „ |
| Lobster . . . . . | 1 „ |
| Oyster . . . . . | 0·03 per cent. |

[1] The definite form of a noun, in the Scandinavian languages, is, as a rule, expressed by suffixing the article, but it is not employed in compound words; *e.g.*—
fisheries of Finmarken: Finmark-fisheries;
islands of Lofoten: Lofot-islands;
district of Romsdalen: Romsdal-district, &c.

away from home to spawn, because if the youngsters were deposited under the paternal roof-tree, and presumed to become big enough to be visible to the naked eye of their unnatural parents, the latter would probably regard them as convenient *hors-d'œuvre.* The question why the fish come to these particular grounds to spawn is, however, a point of interest only; the point of practical importance is that they do come, and that they seem to find the place quite up to their expectations—a satisfactory circumstance no doubt to them, as it is also to those who catch them.

The *Loddefiske*, the other variety of the periodic cod fishery, takes place off the coast of Finmarken, north of lat. 70°. Here the spawning fishery is not of any importance, but after it is over, that is in April, the important *Loddefiske* begins, and lasts till the end of June. The fishery is, indirectly, named from the caplin (*Mallotus arcticus*), in Norway called Lodde. It belongs to the *Salmonidæ*, and is the smallest species of that family, being only from five to seven inches in length. Its home is in the Arctic Ocean, lat. 64° to 75°, but in March or April it appears off the coast of Finmarken, coming there to spawn, and sometimes in such enormous quantities as to form a continuous mass extending for many miles. In pursuit of the caplin come great numbers of gulls and whales, and immense shoals of codfish and haddock, the capture of the two last constituting the *Loddefiske* or Finmark fishery.

## LOFOTEN FISHERIES.

### *Lofoten.*[1]

The Lofoten Islands[2] reside within the Arctic Circle, between lat. 67° and 69°. They are part of a large group of islands arranged in the form of a triangle, the base resting on the Norwegian coast, while the apex stretches away out to sea in a south-westerly direction. The base is called Vesteraalen, the apex Lofoten; the exact number of islands in the group is not known to any man now living: they are of assorted sizes, from Hindö, with its 600 square miles, to Röst, which name is represented on the map by a black dot, and on the Arctic Ocean by 365 islands, one for each day of the year, as the fishermen put it.

The islands are inhabited by the Maelstrom, the Midnight Sun, and a few people 'of no importance.' They are also largely visited by callers belonging to three quite distinct grades of society. First, the tourist (var. *Brit.*, *Amer.*, *et Germ.*); secondly, the cod-fish (var. *G. morrhua*); and lastly the Norwegian fisherman, who has no particular Latin name, but is a very decent fellow notwithstanding.

The tourist, unlike the other visitors, comes to Lofoten on pleasure bent, and ostensibly to pay his respects to the Maelstrom and the Midnight Sun, both unique characters in their way, and quite worth a visit. The Maelstrom (mill race) is near the apex of the group of islands between Værö and Moskenæsö. From the days of the Sagas its reputation has been evil, but its little misdeeds of former times are as nothing compared to the deadly sin it has committed within the last few years, that is, since it went into society. The Maelstrom is one of those unspeakable individuals who have no regular visiting days, and as its habits are most erratic, not a few of its tourist friends call only to find it 'not at home.'

The writer has crossed from Moskenæsö to Værö with a sea so calm that had he not known the fact previously he would never have suspected he was right over the great whirlpool. But, on the other hand, the Maelstrom is never to be depended on, and sometimes when not particularly wanted it is 'at home,' and very much so. Dr. G. Armauer Hansen, the well-known director of the leper hospital at Bergen, gives a graphic account[1] of a somewhat boisterous welcome with which he was once favoured. The following extract is a free translation: 'The waves rose, not as ordinary decent waves with nice, smoothly rounded tops, but as great masses of water, curving, hollow, and foam-crested, suddenly rising, and then collapsing as if on a rock. The skipper did not seem to like the look of things, but after a little hesitation he gave the order, Go ahead. Now we were in for it, and once in there is no turning back; the only courses are to get through, or to get swamped. Fear is unknown to me, but I must own I was not perfectly at ease when one of the great billows happened to collapse quite close to us—a little closer and we would have been gone.'

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[1] In English usually and erroneously written 'Lofoden.'

[2] 'Lofot-islands' would be the correct—but in English, no doubt, unfamiliar—form; we have therefore retained that of 'Lofoten' throughout.

[1] *Naturen*, 1892, p. 271.

The tourist who happens to find the Maelstrom in working order will be quite satisfied, and if he misses that sensation, he is certain of the Midnight Sun, for it is always 'at home' during the season, and ready to welcome pilgrims to its northern shrine, Lofoten. The worship of the Midnight Sun is conducted on good old ways that were familiar even in the days of Noah. These are the libation and the burnt-offering. The former is champagne (exact number of glasses not specified) and—it is not thrown into the sea. The burnt-offering is a hat, preferably new, and in this the devout worshipper bores a hole *secundum artem* by means of a burning glass and the Midnight Sun. These orthodox rites being duly honoured, the pilgrim is at liberty to return to his ancestral halls, where he proudly displays 'the hole' to his astonished and admiring friends, and—goes to buy a new hat.

The writer has no wish to set up as 'the superior person,' but he would venture to suggest that with a certain amount of application and, say, a nail a very good hole may be made in almost any kind of hat; further, this may be done quite conveniently at home: at Lofoten there is another and more worthy form of worship, not on board palatial steamers crowded with chaffing, toast-drinking tourists, whose sole object is to amuse and be amused, but as far possible from 'the madding crowd,' perfectly alone in a small boat out on the sea, or in some quiet solitude upon the shore. There to the understanding mind the solemn grandeur of the scene comes home, never to pass away. The lofty rugged hill-tops of Lofoten all around and the calm stretch of water below lie in a dark-red glow of light, and a perfect stillness, as of death, while to the north the great orb rolls in his majesty along the nadir path. Then only may the eyes of men turn to the sun; and standing alone in that strange light, face to face with the one Awful Presence, man ceases to think, and simply feels that with the silent earth and sea he offers adoration to the Ruler of the heavens, to the grandest work of God.

The Lofoten group of islands and the Lofoten of the fishery officials are not quite the same thing. The former name is applied to the four islands forming the apex of the whole group; while the official name is applied only to their south-easterly shores, facing Vestfjorden and the mainland. The four Lofoten islands consist of East Vaagö, with an area of about 200 square miles; West Vaagö, 150 square miles; Flakstadö, 32 square miles; and Moskenæsö, 80 square miles. These islands lie in 68° lat. They form a pretty compact group, being separated from each other only by narrow sounds, and they are the scene of the great Lofoten fishery, concerning which something may now be said.

The tourist who visits Lofoten in the summer would hardly recognise the place in its winter garb. The Maelstrom is still there, but in a very different mood, and the fierce conflict of its waters is a real and ever-present danger to the fishermen. The Midnight Sun, however, is gone. Sunrise no longer combats sunset, and Lofoten no longer rises from the sea like a magic fairyland of light and shade of every hue. Still she is grand, but with a stern, cold grandeur. Her great mountains are now clothed in white immaculate, and when viewed from a distance they appear, one shining battlement, crowned here and there with giant towers. On coming nearer, however, the great mass of white begins to break up into separate mountain groups; still nearer, darker groups rise up against the bases of the white ones; and when at length the coast is reached these darker hills open out into clusters of small islands behind which the fishing boats nestle in safety from the Arctic storms. Each island group, together with the land behind it, forms a natural harbour, and is known as a *Vær*. These are pretty numerous, there being over forty of them along the Lofoten coast, and they are yet another evidence of kindly Nature's care for the Norwegian. Had the *Værs* been wanting, even with everything else as favourable as at present, there would be no fishery at Lofoten—to throw up artificial breakwaters and harbours there might be a task for gods, but not for men.

Such, then, is the scene that would strike the stranger approaching Lofoten in winter, in the time of the fishing, and, having personally conducted him to the theatre of operations, the writer may now be permitted to introduce the *dramatis personæ*, the cod-fish and the Norwegian fisherman. On the principle of *place aux hommes*, before the cod-fish comes that particular 'lord of creation' who captures him.

### *The Norwegian Fisherman.*

As has been already said the fisherman is not a permanent resident at Lofoten, but like the cod-fish and the tourist he comes there at a particular time and for a particular purpose, which being fulfilled he departs to his own place. That place may be anywhere along the coast, even to the south of Bergen. This fact alone is a grand 'certificate of character,' for the distance from Bergen is nearly 700 miles, and in the winter the regular steamers are unable to cover it in much less than a week. Yet the fishermen do the journey as a matter of course—do it in their small open boats in the dead of winter, when the brief daylight seems to dawn only to fade away, and the darkness, with gales and snowstorms, adds terribly to the dangers of a coast that is difficult to navigate even when illumined by the almost constant summer sun.

The great majority of the fishermen are tall and powerfully built, with strong, deeply cut, often handsome features. They may not seem very active on shore, but on sea they are vigorous and enduring to a degree, and in the face of danger no bolder or more resolute men are to be found. They are not given to much speaking. The sad, stern spirit of the Northern Sea has entered their souls, and they are silent and grave, as becomes men who day by day carry their lives in their hands. The dangers to which the fisherman is exposed are everywhere great, but in the wild seas off Lofoten they are doubly so. Some years ago over 500 men lost their lives in a single day, and on another occasion, in 1893, about 120 perished. Besides these great catastrophes there is a steady drain of life from minor casualties, some idea of which may be formed from the table below.

CASUALTIES OF THE LOFOTEN FISHERY.

| Year | Men engaged | Wrecked | Per cent. | Saved | Per cent. | Loss | Per cent. |
|---|---|---|---|---|---|---|---|
| 1886 | 28,900 | 71 | 0·25 | 57 | 0·20 | 14 | 0·05 |
| 1887 | 28,000 | 174 | 0·62 | 129 | 0·46 | 45 | 0·16 |
| 1888 | 31,900 | 101 | 0·32 | 75 | 0·23 | 26 | 0·09 |
| 1889 | 30,100 | 60 | 0·20 | 48 | 0·16 | 12 | 0·04 |
| 1890 | 30,300 | 39 | 0·13 | 33 | 0·11 | 6 | 0·02 |
| 1891 | 30,400 | 180 | 0·59 | 131 | 0·43 | 49 | 0·16 |
| 1892 | 30,100 | 36 | 0·12 | 28 | 0·09 | 8 | 0·03 |
| 1893 | 26,700 | 187 | 0·70 | 50 | 0·19 | 137 | 0·51 |

### *Fishing Boats.*

The boats used on the Norwegian coast north of 64° lat. are of quite a unique type. They are beautiful craft, exceedingly light and flexible, yet strong enough to stand the strain of the severest wind and weather, even when laden to the gunwale. There are several varieties,[1]

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[1] The chief varieties are:—

| Name | Length | Beam | Pairs of oars | Men | Carrying capacity |
|---|---|---|---|---|---|
| | Feet | Feet | | | Tons |
| Femböring . | 36–48 | 8½–10 | 5 | 6–8 | 7 1,200–2,000 fish |
| Ottring . . | 28–30 | 6–7 | 4–5 | 3–5 | 3½ 600–1,000 „ |
| Trerömming . | 18–20 | 4½–5 | 2–3 | 2–3 | 1 200 „ |

named after the number of thwarts—a method which at once indicates the size of the boat, as the distance between the thwarts is always 36 inches; that is, the length of a barrel.

The boats are fitted with a single mast and square sail—about the best rig for running before the wind—and given this condition they will show a clean pair of heels to almost anything else that sails the sea. Unfortunately it is not possible to be always running with the wind, and when it comes to beating up against the wind the square-sail rig is enough to try the patience of a Job. As a rule there is but one course—the men have to take to the oars—and when they are put to it, the amount of rowing that Norwegian fishermen can get through is something astonishing. Sometimes, however, in heavy weather the struggle proves too much even for them, and nothing is left but to bear away and try to make land somewhere or anywhere.

The Norwegian fishing boat has, however, yet another defect—its instability—and off Lofoten there are few things less desirable than an easily capsized craft. Squalls may be expected at any moment, and they come rushing down from the mountains with most alarming suddenness and force. The writer has seen them lift the timber houses right off their foundations, and toss small boats completely out of the water, sometimes pitching them high-and-dry upon the land. The fishermen are of course quite familiar with these nasty little tricks of the wind, and their skill in meeting them could not very well be exceeded; but so long as they use the present type of boat, accidents will occur—and frequently. That they now do, may be gathered from the fact that during the last ten years no fewer than one-third of all the casualties at Lofoten has been due to boats capsizing.

It may seem astonishing that the fishermen, knowing these things, do not make short work of the offending boats, and provide themselves with a safer form of craft. They are beginning to do so, and especially since a late storm, when it happened that a progressive individual with 'a fore and aft' boat saved it and his crew while all around perished. Still the process is very slow, and in the winter of 1893 out of the 7,000 boats at Lofoten only about 200 were of the new type. The Norwegian fisherman is very conservative in his ways, and he does not see why the boat that was good enough for his forefathers should not be good enough for him. Further, the boat has been his home ever since boyhood; he has grown to love it even with all its faults, and in addition he has a keen sense of the beautiful, and cannot be got to look with favour upon the somewhat unattractive although safe 'fore and aft' substitute. Those who know the artistic merits of the present craft will here sympathise with the fisherman. It is almost worth visiting Lofoten simply to see these boats as they come racing in from the fishing grounds, now rising on the crest of a wave, now disappearing, boat, sail, and all; then, as the distance lessens, the foam is seen flying over the sharp bows as the stem cuts the water like a knife, and the great square sail stands taut to the wind, till rounding up, the craft sweeps into the sheltered water, a perfect picture of graceful ease.

### *The Boats' Crews.*

Nowhere on earth is the 'equality of man' more truly practised than on a Norwegian fishing boat. Birth, wealth, and influence simply do not count, and each man ranks in accordance with one thing only—his personal worth. Very often the man who is the master at home takes the oar on board, while his servant passes to the stern and grasps the tiller, the sceptre of authority. Generally the men come from the same district, sometimes even from the same household; and from apprenticeship onwards they have day by day faced danger together, and—they *know* each other. No formal election is ever required or made, and the skipper (*Hövidsmand*) is simply the man whose strong arm, cool nerve, and ready resource are most to be relied upon in those terrible moments when the lives of all hang on a thread. No commission of authority rests on a base firmer than this: the crew have themselves chosen their captain, and his word to them is absolute, for in the face of danger everything depends upon instant, unquestioning obedience to his orders.

The post of *Hövidsmand* is thus one that can be earned only by true and well-tried worth. It is the aspiration of every member of the crew from boyhood onwards, but when it comes it brings a terrible responsibility. The chosen captain knows that his slightest failure or error of judgment may mean, not only the lives of the crew, but that Nemesis that is ever with the fisherman, the misery that may be worse than death to those at home—the little ones, wives, and sweethearts.

The *Hövidsmand's* work is thus by far the hardest; nevertheless honour is its sole reward, for not one penny extra of the joint earnings goes to the holder of the post. By an unwritten law the *Hövidsmand* retires when he reaches his fiftieth year, a younger man passes to his place, and he who yesterday held absolute command gives as absolute obedience to-day.

### *The Fishing Tackle.*

*Nets.*—Three different kinds of tackle are used in fishing for cod: the net, the longline, and the handline. The net is considered a *recent innovation*, as it has been used only since 1685. It was not by any means a favourite at first, but has now established a firm footing in the good graces of the fishermen. The boats used for the net fishing are the *Femböringer*, the largest form. They have a crew of six or seven, and carry from ninety to 120 nets, of which each man contributes a share. The net is about 30 yards in length, and 4 to 6 yards deep, with meshes about three inches square, just enough to permit the codfish to poke his nose through; and when he has done so, he finds he can get no further, nor can he get back. A number of these nets are linked end to end, so as to form a continuous net, often over half a mile in length; and when the boat arrives at the fishing ground the net is run out, one margin being made to sink by stones or pieces of iron, while the other is kept up by floats, hollow glass globes, attached to it at intervals. The net, thus suspended vertically, forms an obstruction where the codfish, no doubt, considers he has a 'right of way,' which it is his duty to mantain, as he does, but with results more disastrous than 'prosecution according to the law.'

*The Longline* was introduced some time ago. The writer would rather not take the responsibility of saying how many centuries. The boat used for this is the *Ottring*, with a crew of three to five men, and the tackle is simply a strong hemp cord to which hooks are attached by means of short cotton snoods. The hooks are about four feet apart, and a line bearing 480 of them is called a stamp, and lies baited and ready for use in a tub made by cutting a barrel in two. The line is generally run out across a current, and allowed to sink to the proper depth, where it is suspended by floats. When one stamp is exhausted, another is tied to its end, and this is continued till miles and miles of line have been run out, so that the name 'longline' is by no means a misnomer.

*The Handline.*—The fishermen who cannot afford a *Femböring*, or even an *Ottring*, content themselves with a smaller boat and handlines. These are about a hundred fathoms in length, with baited hooks attached to the end of them.

The number of fishermen at Lofoten using these respective varieties of tackle is shown in the following table:—

| Year | Nets | Longlines | Handlines | Total |
|---|---|---|---|---|
| 1889 | 11,628 | 15,793 | 2,662 | 30,083 |
| 1890 | 13,312 | 14,907 | 2,105 | 30,324 |
| 1891 | 13,529 | 14,393 | 2,456 | 30,378 |
| 1892 | 12,994 | 14,672 | 2,426 | 30,092 |
| 1893 | 11,410 | 13,231 | 2,042 | 26,683 |
| Average | 12,575 | 14,599 | 2,338 | 29,512 |

The tackle forms a very heavy item in the fisherman's annual budget. This is due to the fact that not only is it expensive to begin with, but it does not last long, for the sea seems to delight in taking liberties with fishing gear, and liberties of a most objectionable nature. Sometimes the strong currents carry nets and lines clean away; or it may happen that they are very considerately returned to land a few hundred miles off; but this is rare, and as a rule when the sea once gets them into its possession it keeps them. Storms cause an even greater amount of loss, for they frequently come on when the fishermen have their tackle down, and then there is no choice but to leave nets and lines to the tender mercies of the sea, which entreats them shamefully. Generally when the poor fellows do succeed in getting their gear up again after a storm, it is only to find it so hopelessly mixed and broken as to be almost, or quite, beyond repair. The following table will give an idea of the amount lost in this way by the Lofoten fishermen:—

| Year | Loss of nets | Loss of longlines | Damage to nets | Damage to longlines | Total |
|---|---|---|---|---|---|
| | £ | £ | £ | £ | £ |
| 1889 | 8,400 | 6,000 | 16,000 | 4,500 | 34,900 |
| 1890 | 1,700 | 5,800 | 15,000 | 3,000 | 25,500 |
| 1891 | 6,600 | 4,500 | 14,000 | 3,500 | 28,600 |
| 1892 | 4,400 | 4,500 | 11,000 | 4,200 | 24,100 |
| 1893 | 4,600 | 5,300 | 11,500 | 6,000 | 27,400 |
| Average | 5,140 | 5,220 | 13,500 | 4,240 | 28,100 |

### *Bait.*

The anatomist tells us that the cod-fish has no brains to speak of, but he is not on that account so foolish as to try to dine off iron hooks *au naturel*. His taste has, therefore, to be studied by the line fisherman, and the succulent dainties that meet with approval have to be procured and paid for—another important item in the bill of expenses. The dish to which the cod is most condescending is his not very distant relative, the herring, and he prefers to have him fresh. But, alas! a fresh herring at Lofoten in January would be about as astonishing as the right man in the right place. In fact, whenever the shoals of cod begin to arrive all the other fish seem to take fright and their departure, and in the hauls nothing is to be seen but cod, cod everywhere. Fresh herring, however, must be had somehow, and had they are, by a most ingenious expedient.

It so happens that in the autumn great shoals of herring visit the Norwegian coast to the north of Lofoten, and as they enter the numerous fjords, sweep-nets are carried across from shore to shore behind them. Their retreat to the sea is thus cut off, and the ends of the sweep-net are gradually drawn along the shores towards the top of the fjord. The herring are of course driven upwards by the advancing net, till at length the end of the fjord is almost reached, and there they are confined in a space so small that they have sometimes scarcely room to move. They can now be taken out of the water without the slightest trouble, and just as they are required. Some of them are immediately disposed of, but as herrings are of little value at that season, great numbers are kept in confinement till the beginning of the year, when they are sent south to Lofoten, and sold at high prices to be used as bait. The quantities of bait chiefly used at Lofoten are shown below:—

| Year | Fresh herrings | Salted herrings | Mussels | Caplin | Total value | Average for each line-fisher |
|---|---|---|---|---|---|---|
| | Barrels | Barrels | Barrels | Barrels | £ | £ s. d. |
| 1889 | 25,000 | 6,200 | 2,000 | 1,450 | 16,400 | 1 0 9 |
| 1890 | 30,000 | 2,000 | 3,000 | 4,000 | 28,300 | 1 17 11 |
| 1891 | 10,000 | 5,000 | 1,300 | 5,000 | 16,100 | 1 2 4 |
| 1892 | 6,000 | 10,000 | 1,000 | 4,000 | 16,100 | 1 1 11 |
| 1893 | 5,000 | 9,400 | 600 | 11,500 | 11,700 | 0 17 9 |
| Average | 15,200 | 6,520 | 1,580 | 5,190 | 17,720 | 1 4 2 |

### *Social Customs.*

On his arrival at Lofoten, the fisherman makes for one of the *Vœrs*, or natural harbours, and there he establishes his headquarters for the ensuing campaign against the cod-fish. Every *Vœr* is in the hands of one or more proprietors, who purvey to the fisherman such things as are understood to be the necessities of life in these regions, and who also buy from him the fish that he is fortunate enough to catch.

Each boat's crew is provided with a dwelling, which, however, cannot be described as 'that handsome and commodious residence.' It is, in fact, a mere hut, built of wood, roofed with birch bark, and divided by a partition into two rooms. The outer room is generally pretty well occupied by fishing tackle, and the inner by four to six men, a cooking stove, a couple of benches, and two bunks arranged, cabinwise, one above the other. Perhaps the most interesting thing about these rather simple domestic arrangements is the door-latch. This is a wooden lock constructed on the 'Brahma' principle, but of very ancient origin; and to those who are interested in ethnological matters it may be news to hear that the primitive lock of the Syrian peasant has practically an exact counterpart in use at this present day within twenty-five degrees of the North Pole.

The Lofoten fisherman is his own cook, and the results of his efforts would probably seem very dreadful to a French *chef*; but he himself 'takes' them quite calmly, and thrives upon them. His bill of fare shows three principal items: dried meat, chiefly mutton; *Lefse*, a kind of soft flat cake made from oatmeal; and *Fladbröd*, a hard leaf-like bread, also of oatmeal. These are helped out, or down, by cheese and butter, but, in common with his brethren of the craft in other lands, the Norwegian fisherman despises fish as food for himself. When he is particularly hard up, he does, it is true, condescend to a fish diet, and even at other times he will partake of a dish prepared from cod's tongues and *Fladbröd* soaked in the oil from the freshly boiled liver, which he considers a dainty 'fit for gods or men.' Coffee is his chief drink, and for reasons that we have already indicated, and over which he has no control, the Lofoten fisherman is a 'total abstainer.'

The earnings of each boat are divided among the members of the crew, who rank as whole-lot men, three-quarter-lot men, and half-lot men, according to individual experience and fitness for the work. The *Hövidsmand*, as such, gets no larger share than any of the others. Boys during their apprenticeship generally have the proceeds of a particular net set aside for their benefit. When a boat happens to be short of hands, men hired and paid by the day are obtained from a number of fishermen—between two and three thousand—who for one reason or other have no boats of their own, but who are always sure of work, Lofoten being a labour paradise where the army of the unemployed is an unknown evil.

Serious crime is also practically unknown,[1] a very remarkable fact when we consider that between twenty and thirty thousand men congregate at Lofoten every season, and there pursue a calling which is bound to give rise to almost constant disputes. These do not result in the gravest consequences, simply on account of the mutual forbearance and good sense displayed by the different boats' crews. The magisterial functions are exercised by the Inspector-General of the Fishery, who is always a naval officer, and his subordinates. He sees that the fishery regulations are carried out, punishes offenders by fines, and acts as arbitrator in matters of dispute that the men fail to settle for themselves. Should his decisions not be acquiesced in, the cases may be carried before a specially appointed judge; if serious crimes do occur, they are sent to the regular courts of justice. The most frequent offence is theft, not on land, but on sea, when the tackle of different boats gets mixed, and gives a chance to those who find it difficult to distinguish between their own and their neighbour's fish. Needless to say, sinners of this kind are seldom Norwegians, but Finns—Laplanders—of whom a few are always to be found at the Lofoten fishery.

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[1] During the last ten years the average number of grave offences was only seventeen *per annum*. Of these thefts averaged eight, forgeries four, and in the whole period there was not a single case of murder, and only one of manslaughter.

### *The Cod-fish.*

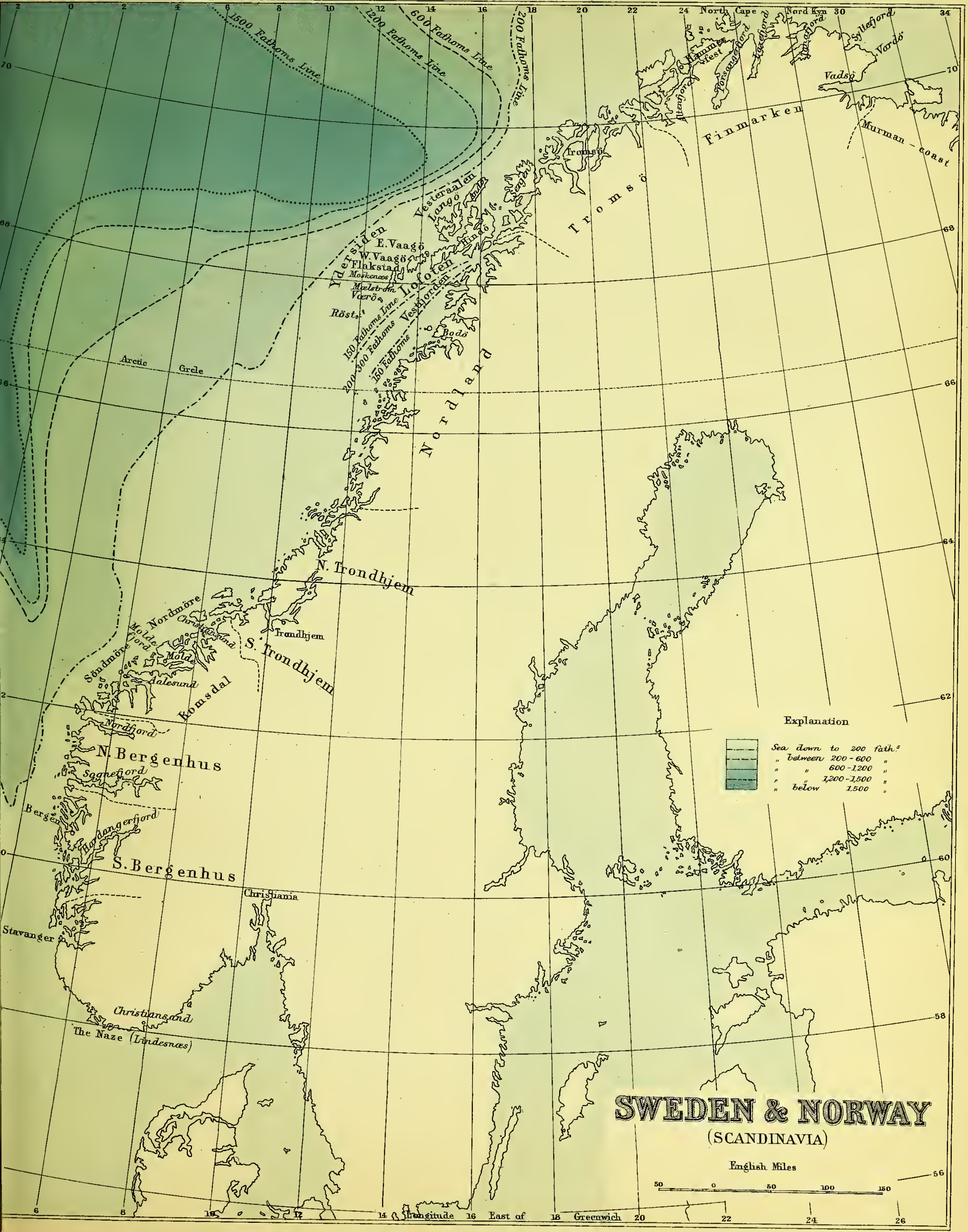
Of the three classes of visitors to Lofoten the cod-fish are the oldest established. Their visits are mentioned in Eigil's Saga—*circa* 930—and since that time, so far as records enable us to judge, they have arrived year by year with the regularity of the winter season, and in such multitudes as to defy computation. Why they have elected to go to Lofoten in preference to other places is a question that presents no difficulty to the scientific mind: the cod visit the Norwegian coast for the sole purpose of spawning, and select the regions that are specially sheltered, so that there the ova may lie in safety until they are able to shift for themselves.

This seems a very good theory, only it happens to be of the kind that requires 'facts made to fit them.' The cod-fish does not care much for its young except as tit-bits, to be swallowed whenever they come within reach, and it is rather too much to ask us to believe that a parent of this type is likely to trouble about the most suitable nurseries for its little ones. Of course we admit that natural selection may teach even the cod-fish, but there is yet another and absolutely fatal objection to the scientific theory. The seas around Lofoten are by no means quiet and sheltered—in fact they are the most exposed and stormy on the whole coast. Elsewhere the inner channel is protected by the great *Skjœrgaard* breakwater, but the Lofoten group of islands stretch right out into the open sea, and get the full benefit of every breeze that blows, while the *Vestfjord*—where the spawning chiefly takes place—is simply a huge funnel into which the Atlantic storms sweep without obstruction, and where they rage after their own sweet will.

The real explanation of the preference the cod-fish show for Lofoten is probably to be found in the arrangement regulating the flow of the ocean currents. Besides Lofoten there is one other point to which the cod flock in enormous numbers for the purpose of spawning: that point is Romsdalen, about 450 miles to the south of Lofoten. Now if these two places had something in common, something not shared by the rest of the coast, it would be but reasonable to look to that for a possible solution of the problem, and it so happens that this is exactly what they *do* have. As has been already stated, the water close to the mainland is of great depth, but beyond this the sea-bed rises into a bank the outer edge of which suddenly slopes downwards into the deep bed of the Atlantic and Arctic Oceans. This slope is much more sudden immediately to the seaward of Lofoten and Romsdalen than elsewhere, and at these two points the deep bed of the ocean runs in towards the land, forming two entering angles or bays. It would be remarkable were it a mere coincidence that these bays occur just at the places selected by the cod-fish, and not elsewhere, and the question that naturally arises is, In what way can they influence the choice of spawning grounds?

The chief end of all the lower forms of organic life is food, and as the cod-fish is pretty low down in the scale, we should expect that the question of what he can get to eat bulks largely in his estimation—much more than the welfare of youth, even as applied to his own children. His intellectual development having reached that stage where the guiding principle in life is the gastric juice, he is likely to choose his home just where he can most easily fill his stomach. But even to him a plentiful supply for the digestive organs is not everything; cold-blooded as he is, he dislikes chilly waters as much as tropical currents, and, no doubt, his idea of perfect bliss is to combine the pleasure of taking his ease in a properly-cooled current from the south, with the profit of having there the food of the deep waters from the north flowing into his mouth. This combination of comfortable circumstances is likely to be found along the edge of the great bank outside the whole coast of Norway, but the 'bays' which have been referred to are probably the means of sending a much more plentiful supply of fish food to the parts of the bank in their immediate vicinity than is to be found at any other part; thus, these places can support greater multitudes of fish than could exist anywhere else. The fish food is not altogether devoid of interest. It originates in a protoplasmic basis which serves as nutritive material for immense multitudes of amœboid animals belonging to the protozoa. These form a suitable dietary for flagellata, radiolaria, and other infusoria, which in their turn support amphipoda, decapoda, isopoda, and other crustaceous animals which are the cod's delight. The series is somewhat like an epitome of the evolution of the lower forms of life, and, as if to complete the analogy, the simple protoplasmic substance from which the whole is built up is as mysterious in its origin as life itself. In fact, no man knows anything as to how the protoplasm comes into existence. It seems to be manufactured somewhere in the polar regions, and in quantities that almost exceed belief—we have been told by skippers who frequent the Arctic seas that they have sailed through such viscid masses for days together. The Arctic current comes from the polar regions down to Norway, but is warded off the coast by the precipitous wall of the great bank, up to the edge of which it does not reach, and along which, therefore, the cold current runs southwards, charged with the rich food for the swimming population of the ocean; but this current is too cold for them to live in. The Gulf Stream, however, from the tropics, flowing on the top of the cold current towards Norway, establishes that happy combination of circumstances so necessary to the well-being of the cod-fish. On account of the opposite directions of the two currents, the upper strata of the Polar current must get mixed with the lower strata of the Gulf Stream, and consign to the latter some of the feeding stuff it contains, which in this way is carried back to the bank; and thus charged and cooled, so as to be comfortable to the fish, it rises to a sufficiently high level, flows over the edge of the bank to where the cod are awaiting its arrival; fills the basin, the ‘inner passage’ and the fjords on the other side of the edge. Where the wall of the bank runs in a tolerably straight line, this mixing of the two currents must be less marked, and the lower strata of the Gulf Stream are not impregnated with sufficient food to sustain any unusual abundance of fish life; but the case is different where there are extensions of the deep ocean bed into the submarine plateau off the coast, forming the aforesaid bays or nooks. Of such, there is one opposite Lofoten, and another opposite Romsdalen, as will be seen from the accompanying map. The deeply-situated Arctic current enters these bays, and whilst elsewhere it is turned off into the ocean by the face of the plateau, here that is impossible. The current, in fact, is caught in a sort of trap, and as it flows on towards the apex of the nook, any escape back to the Atlantic becomes more and more difficult. Doubtless, a certain proportion of the inflowing Arctic water does escape by means of a deep back current, and, indeed, it might all escape in this way if the apex of the bay were sufficiently rounded. It is *not* rounded, however, but the very opposite, viz., an acute entering angle; and when the current reaches this, there is but one means of egress. The water pressure behind forces it on, and as there is no getting backward, it is compelled to rise up towards the surface, where, mixing with the warm surface current (the Gulf Stream), it flows over the edge of, and crosses, the bank.

In this way it happens that the waters in the Lofoten and Romsdal regions are mixed with a greater portion of the Arctic current than the waters at any other point of the coast, and these regions are therefore favoured with a supply of the fish food which the Arctic current brings. Hence the cod-fish and the cod-fisheries of Lofoten and Romsdalen. On the rest of the Norwegian coast the waters are by far not so rich in fish food, *ergo* there are no cod-fish to speak of, and no cod-fisheries of any



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importance. This theory receives a very remarkable corroboration from observations of the sea temperatures at Lofoten. The mixture of the two currents could not, from the point of view of the physicist, be a perfect mixture. What would be expected in these regions would be the presence of a number of more or less well-defined currents of different temperatures. The series of observations that have been taken for many years show that this is exactly what obtains at Lofoten, and shows, moreover, that the cod-fish are to be found only in the cold, and therefore presumably Arctic, currents with a temperature of about 5° C. (41° F.)

### *The Supply of Fish.*

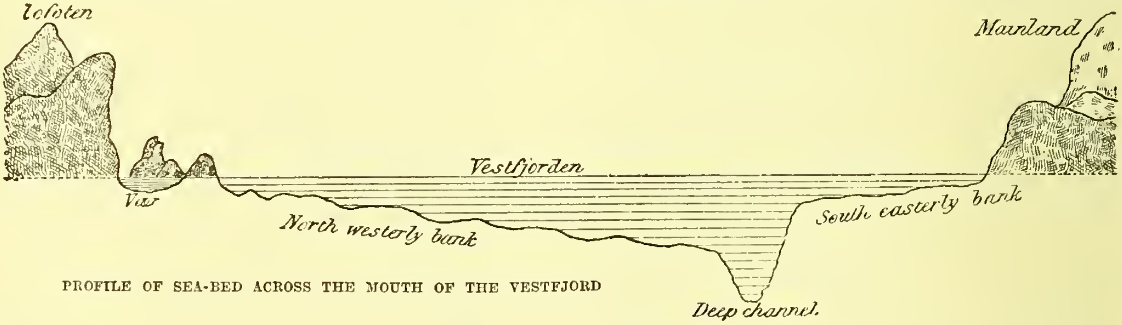
According to some authorities the cod-fish are practically numberless, and no inroad that man can make upon them is of any moment. Others, again, think that they are by no means so numerous, and, indeed, that their total destruction is not improbable if the hitherto reckless slaughter be not checked. With these two conflicting opinions it is rather difficult to come to a conclusion. An absolutely certain conclusion would require a regular census of the cod-fish—to take which would be somewhat difficult. An approximate idea of the matter may, however, be formed from the following facts within our knowledge.

The cod do not come to Lofoten in one body, but in numerous separate shoals. This, in all probability, is due to the varying distance the fish have to travel from their homes across the outer bank, the detachments from the nearer colonies arriving at the beginning of the season, while those which appear afterwards have had a longer journey. On the banks these different bodies of fish seem to keep to themselves; and when the spawning is finished each shoal again makes for its own particular habitat. In the year 1887 it so happened that the weather of Lofoten was exceedingly stormy during practically the whole of the fishing season, and, whether on that account or not, a rather abnormal thing happened: one of the shoals of cod left the banks and entered the Östnæsfjord in the island of East Vaagö. It was a most fortunate occurrence for the fishermen, for they were able to let down their gear in the sheltered waters of the fjord when it was impossible for them to venture out to the banks. The shoal entered the fjord early in January, and as soon as the news got abroad, about 2,500 boats congregated at the spot, and were successful in catching over *thirteen millions* of fish. This immense number was, however, a mere nothing as compared to the total in the shoal.

Östnæsfjord is an inlet nine miles in length, and on the average one mile wide, and its area may be taken at nine square miles. Over all this, between the depths of sixteen and forty fathoms, the fish were simply packed together, not exactly like sardines in a box, but supposing we allow each fish ten times its bulk of water, then the cubic space would contain *ten thousand million.* Even supposing that were divided by ten, the number of fish caught, immense as it was, would obviously be far too small a fraction to make any impression whatever on the main body. Now, this was only a single shoal out of the scores, or perhaps hundreds, of shoals *on the banks*; for whenever there was a lull in the storm, so that boats could venture out to the open sea, other shoals were found, abundantly, all over the 1,200 square miles of the inner banks, as well as on the extensive banks which lie to the outer side of the Lofoten Islands and are collectively known as Ydersiden. It is, of course, very difficult to form even a rough estimate as to how many shoals might have been present, but certainly the number must have been considerable. Bearing this in mind, and using as a basis for calculation the conception that we have been able to form of the immense quantity of fish in a single shoal, we are left with but one possible conclusion—that the cod comes to Lofoten in numbers which, for all practical purposes, are limitless, and on which all the efforts made by man cannot produce any effect worth speaking about.

This being so, it would be simply purposeless to impose any limit to the number of fish to be caught in each season. The real fact of the matter seems to be that, amongst the many enemies of the cod, man is of very little account. The female cod-fish produces every year about 100,000 eggs for each pound of its weight, or in other words each average Lofoten 'spawner' is responsible for a family of 1,200,000 every season. So far as the fishermen are concerned, all these have a chance of becoming mature cod, with the exception of about half a million gallons of roe which they take annually. This seems at first sight a fairly large quantity, and it is in reality more than that yielded by all the other fisheries in the world put together; nevertheless it is a mere drop out of the bucket when compared to the total amount, and were the other enemies of the cod as futile in their efforts as man, the whole sea from the North Pole to the South, would be choked with them in a few years. Fortunately there is no danger of this, for the ova, the fry, and the fish are being constantly kept within reasonable bounds by an immense multitude of the denizens of the deep, from the whale downwards; and the aid that man can give them is to be looked upon, apart from its material results, as a praiseworthy, although perhaps feeble, effort to help Nature in maintaining the 'balance of power.'

In size the codfish vary but little; those caught in nets are, on the whole, somewhat larger than those taken by the hook. The former average 32 inches in length and 12 pounds in weight, the latter 30 inches and 10 pounds. The liver of the net fish averages 11¼ ounces, and of the others 9½ ounces, while the roe and milt weigh 20 ounces and 13 ounces respectively. Marked exceptions from these average sizes are rare, but, of course, they are occasionally found. One caught at Lofoten in 1888, and sent by us to the exhibition at Copenhagen, may be taken as about the maximum size of *Gadus morrhua.* It measured 4 feet 11 inches in length, over 3 feet in girth, and its weight was rather over 91 pounds.



PROFILE OF SEA-BED ACROSS THE MOUTH OF THE VESTFJORD

### The Fishing.

*Locality.*—In order to understand the *modus operandi* of the Lofoten fishermen, it will be necessary to give a short description of the Vestfjord, the region where the fish are mainly caught. A glance at the above sketch will perhaps explain the peculiar formation more plainly than words. The deep channel to which we have several times referred sends numberless branches into the mainland, several remarkable instances of which we have already mentioned, such as Hardangerfjorden, Sognefjorden, and Trondhjemsfjorden. The Vestfjord is another of these deep inlets, running landwards from the main stem of the deep channel. It separates the Lofoten Islands from the mainland, and cuts into the latter almost up to the Swedish frontier. At its entrance to the Atlantic it is fifty-five miles wide, but of this only the central part is 'deep channel,' the rest being 'banks.' At its outer end the channel is about 200 fathoms deep, but farther on it gradually slopes down to 300, or even 400 fathoms. Its width, at the top, is about nine miles, and it is bounded on either side by precipitous natural walls, from the edges of which gradually rising banks stretch, on the north-westerly side towards the Lofoten Islands, and on the south-easterly towards the mainland. The channel itself runs nearer the mainland, and its enclosing walls are not equally high: these two circumstances establish a marked difference between the north-westerly and the south-easterly banks. The former, the Lofoten, has at the mouth of the fjord a width of about 30 miles, while the latter, the landward bank, has only 16, both, however, tapering towards the head of the fjord; furthermore the Lofoten bank is, at the edge of the deep channel, about 150 fathoms below the surface, and thence rises gradually towards the Lofoten Islands; the gradient is, indeed, so regular that if lines representing the different depths from 50 to 150 fathoms were drawn from the apex of the bank, seaward to its base, they would spread out in almost geometrically equidistant rays. The landward bank, on the contrary, forms a higher plateau, the soundings at the edge of the channel being only 30 to 50 fathoms, and the water is, therefore, more uniformly shallow all over this bank. The difference in their formation, and the sea temperatures dependent thereon, are probably the cause of the fisheries taking place on the regularly sloping *Lofoten bank*, and it is on it only that the cod-fish are found. There are no fisheries on the other bank towards the *mainland* of Norway.

*Fishing Operations.*—The vanguard of the shoals of cod appears in the Vestfjord with remarkable punctuality in the first week of January, and the fishermen who reside in Lofoten immediately commence work, and prosecute the fishing as soon, and often, as the weather permits.

The campaign commences by finding out if the fish have arrived, and, if so, where they are. This is done by setting lines, which extend, obliquely, from the surface right down to the bottom of the sea, and when the cod begin to 'attach' themselves to these lines, not only is their presence ascertained, but also the exact level at which the shoal is swimming. This is also done later in the season, when the track of a shoal has been lost or the arrival of new shoals is expected. By the end of the month most of the fishermen from other districts have assembled, and the fish begin to arrive in increasingly larger shoals; but they are not in full force before the first week in March, and from that time until the end of the month the fishing is at its best. In the latter part of March the spawning commences, and then the fishing comes, practically, to a temporary standstill.

The cause of this is simply that the fish are too much absorbed in their spawning operations to care for the most tempting bait, or even to move about and so enter the nets. During the process the males separate from the females, not from any sense of delicacy or decorum, but in obedience to a natural law, which has made the ovum of the cod specifically lighter than the sea water. It thus tends to rise towards the surface when spawned. The male fish take up a higher level in the water than the females, and there discharge the milt, by which the ova are impregnated while rising nearer the surface. The spawning occupies only a few days, but the mass of ova and milt liberated is enormous, and sometimes causes the sea for miles around to assume a milky appearance.

After some days devoted to spawning, the fish again become lively, and, although they now turn their noses homewards, are quite willing to take the bait or go into the nets. By degrees, however, the fishing becomes poorer, and at the end of April, sometimes earlier in the month, it is brought to a conclusion.

The Lofoten fishery, as we have already

stated, is under Government supervision. The official staff consists of an Inspector-General, one or more judges, about half-a-dozen medical men, and a number of petty officers—in all about fifty men; besides several clergymen who are commissioned to look after the spiritual comfort of the fishermen. A grant of about 2,000*l.* is voted by the Parliament to defray the expenses of this supervising staff. The Norwegian Parliament does not generally tighten its purse-strings where the public good is involved, but here its generosity is certainly not conspicuous. The grant is miserably inadequate, and the result is that the 'superintendence' of the fisheries is chiefly limited to office work, making out statistical tables, and sending telegrams, regarding the prospects and progress of the fishing, to the several *Værs* and to the outside world. Such a thing as maintaining respect for the law on the sea is almost entirely beyond the power of the officials, because the only means of locomotion granted to them are a few small row-boats, the Inspector-General's repeated requests for a small steamer having been persistently ignored. The only power which the Government staff have to enforce fishery laws is such as can be wielded from *terra firma*. One of these prohibits the boats from leaving in the morning until the superintendent in charge of the *Vær* flies a signal: this law is made in order to prevent the too enterprising crews from going out ahead of the others and helping themselves to more than their own share of the spoil. Another law provides that all fishing-gear must be taken out of the water on Saturday, and not set again before Sunday evening. This regulation is a concession to the religious feeling of the majority of the fishermen, and, of course, to their dislike at seeing such as think otherwise profit by their wickedness. It, however, can hardly be enforced by the land-tied supporters of the law, but, nevertheless, it is seldom infringed. The would-be Sabbath-breaker knows that the eyes of the righteous will mark his evil deeds and that they will straightway be reported to the inspector, who, unless he can be persuaded that 'wind and weather' did not allow of the lines being lifted, will administer to the sinner his due reward.

Directly the signal is hoisted in the morning, each boat makes for the spot where the gear was put down the previous day, and if the haul is satisfactory, the nets and lines are again put down at the same place. Should the catch be meagre, or worse, still, if the men draw a 'black net,' as they call it when the silvery glitter of the captive fish is conspicuous by its absence, then it is evident that the fish are going or gone, and the question is—where? Now it is that the *Hövidsmand's* qualifications are put to the test. The results are in some cases very remarkable—a number of the skippers, over and over again, year after year, know how to choose the exact place, while others search in vain for the fish. This may be experience, or innate instinct, or something else, but not chance—that might explain an occasional stroke of luck, but not a long-continued series of successes.

*Deep-sea Temperature.*—The movements of the cod have always been very puzzling. Sometimes the shoals lie deep down and so densely packed that, according to the fishermen, the lead will not sink through them. At other times they spread themselves out in a thin layer at some particular depth; and so thin, indeed, may this layer be that rich hauls are made from nets and lines which happen to be at that precise depth, while not a fish is caught by tackle set five fathoms deeper or higher. In some seasons the cod will not come near land, but stick to the deep water near the edge of the bank; in others they come close up to the islands, and may be taken at the depth of a few fathoms. Again, for a period of several years, the shoals chiefly visit East Lofoten and then for a similar period they betake themselves to West Lofoten. Captain Juel, however, is of opinion that probably every season there are fish in plenty at both places, but that there is an apparent scarcity of fish at either the one or the other, simply because there is a scarcity of men to catch them. There is no doubt that the fishermen are obstinately tenacious of antiquated opinions. If they think there will be an East Lofoten fishery, there they assemble in great force, and, of course, that year turns out an East Lofoten season as they expected. What fishing there is at West Lofoten may be very good, but the men, like Louis XIV., stick to the principle, *j'y suis, j'y reste.*

The causes of the irregular wanderings of the cod have been the object of much speculation. One idea suggests that the temperature of the water influences the sudden and unexpected movements of the fish, and in 1877 Captain Juel, then Inspector-General of the Lofoten fishery, commenced a series of observations of deep-sea temperatures. They were carried on by him every year so long as he continued in office. The results were rather conflicting, but still, in his final report to the Government, he says that 'the experiences from this winter [1881] appear to confirm the belief that the temperature of the water influences the fishery in a marked degree.' Captain Juel was greatly hampered in these investigations by want of funds. The Government had some time before spent money on some fruitless scientific researches for the same purpose, but in a biological direction, and they did not feel inclined to give further financial support to anything of a similar nature. The investigations were, therefore, extremely limited; indeed, Captain Juel had only one deep-sea thermometer at his disposal, and that a borrowed one. Comparatively few observations could thus be taken, and scarcely any were obtained at places where the fishing was actually in progress. Captain Knap, who succeeded to the Inspectorate, continued the investigations for a time, but becoming discouraged at the scanty support accorded to him, and the consequent barren results, he let the matter drop, his last few observations being taken in 1886.

We were naturally much interested in an investigation which might prove to have important practical results on the Norwegian fishing industry, and when informed that the observations under Government auspices were to be abandoned, we determined to take the matter up ourselves, and to work it out in a more practical way.

The results obtained up to this time, and chiefly from the praiseworthy efforts made by Captain Juel, seemed to show that currents of different temperatures were to be found, and that these may change from day to day in direction and in depth, in extension and in form. His tables, for instance, show that on a certain day there was at the place of observation a current of temperature 5°·25 at the depth of 60 fathoms; next day this current had risen to 50 fathoms, and on the following day it had risen still higher, to 40 fathoms. At the same time another current was running immediately above, and this had a much lower temperature, 1°·75 to 2°·15.

It then appeared to us that if these currents, distinctly localised and distinctly differing in temperature, did in reality influence the movements of the fish, then there was only one method of investigation which was likely to be successful. If the cod followed by preference a current of a certain temperature, it was clear that the best, indeed the only practical, way to arrive at proof or disproof was to make a long series of observations of the temperature of the water *where the shoals were found.* If they were more or less constantly in water of a certain temperature, but not in adjacent currents of lower or higher temperature, then we might reasonably conclude that they had a preference for this particular temperature, and —the point of practical importance—that they would, in all probability, be just where a current of the proper temperature was found.

This deductive method was obvious, but no attempt had yet been made to carry it out. It required, of course, that the investigations should be made on the spot where, and at the time when, the fish were being caught. We therefore selected one of the most intelligent of the men, the *Hövidsmand*, Edvard Meisfjord, instructed him as to what we wished done, and presented him with the necessary apparatus. We further gave him a hint to look out for the fish in water between 4° and 6° of temperature, and then left the matter to work out as an object lesson, in one way or other, for the fishermen. The event proved our selection to have been a most happy one. Meisfjord took to *scientific fishing* with intelligence and with the greatest interest. He regularly found the fish in water from 4°·75 to 5°·25 temperature, and he caught that year no less than 13,000. The following year, 1887, he was equally successful, and uniformly hauled in a rich catch, even when boats all round him were having nothing but 'black nets.'

This was too much for the other fishermen. At first they had been inclined to sneer at Meisfjord and his instruments and new-fangled ideas, but now they began to see that there must be 'something in it' after all, and in the following season, 1888, they veered round from scoffers to humble disciples, and taking advantage of the formerly despised novelty, they crowded upon Meisfjord's boat, so that he could hardly get room to set his nets on account of the other boats pushing in, to place their gear in the neighbourhood of his.

In the official report of that year's fishery the Inspector-General says: 'A large number of the more experienced and able fishermen are now fully alive to the great importance of this subject, and have become desirous of using deep-sea thermometers. The expense of procuring them, however, is more than they can afford, even should their use soon repay the outlay. Much would be gained if, by a grant from the public funds, a few instruments could be provided for distribution amongst the several *Værs*.' The Inspector also sees now (quite in accordance with our conclusions) that the observations of temperature must be made in combination with the actual fishing. It is rather amusing, further, to notice that the Inspector places the credit of the 'discovery' that the fish prefer a temperature of 4° to 5° to the observations *made by the Inspectorate*, evidently forgetting that the Government officials, three years earlier, had given up all hope of achieving their object, and had discontinued their investigations in despair.

The appeal thus made to the public funds was responded to, but not extravagantly. 'The Society for Promoting the Fisheries of Norway' graciously placed *three* thermometers at the disposal of the Inspector. These were handed over to three well-known *Hövidsmænd*, and in the report of 1889, the Inspector-General summarises the results:—

'It seems more and more evident that the temperature of the water plays a very important part in determining the success of the Lofoten fishery, and probably this is also the case in our other large cod-fisheries. The fishermen seem now one and all to have this conviction brought home to them, and requests for loans of thermometers were constantly received. . . . The result of the fisheries this year could not have been so good had it not been for the guide the fishermen had in the thermometers.'

In the next year, 1890, the fish happened to come close to land, and the richest fishing frequently took place at a depth of from five to ten fathoms. Thermometers were therefore not used by the fishermen, but the Inspectorate now resumed the investigations they had allowed to rest since 1886. The observations made were but few, and in the report of that year no reference is made to their having been undertaken 'in combination with the actual fishing'; in fact, the temperature at five to ten fathoms does not appear to have been once taken.

This sudden recrudescence of official activity did not in any way influence the course of observations carried out through Edvard Meisfjord, and for comparison's sake we may give extracts from some of the reports he sent us.

In the beginning of February 1889 he tried the temperature at 60 fathoms, and found it was not higher than 2°·5 to 3°, and he caught only 150 fish. He then moved farther out to a part of the bank where the temperature at 80 fathoms was 4°·5 to 5°, and here he caught 1,100 fish. He was the only one of all the fishermen who tried so far from land, and the others, without exception, had a catch that was very poor. As soon, however, as they learned where Meisfjord had spread his nets they all made for the spot he had selected, and there they obtained splendid hauls up to the middle of March. At this time the temperature nearer land rose to 5° at 70 fathoms, and Meisfjord removed his nets higher up on the bank, and again obtained abundance of fish; while at the former place, where the temperature had risen to 6°, no fish were to be had. This lasted for eight days, and then he observed that the conditions again changed. Water of the requisite temperature was again found, as it was from February to the beginning of March, farther out near the edge of the banks, and here, as it is now almost needless to say, a rich fishing was obtained, which lasted throughout the remainder of the season. It is of this year's fishing that the Inspector says, in his report just referred to, that the result of the fisheries could not have been so good but for the use of thermometers.

The report received in 1892 contained some additional points of interest, which we may mention. There were very few fish in the Stamsund region of the banks that year, and the temperature of the sea did not rise above 3°·5, with the exception of two nights in March, when 5° was found at 60 fathoms. On these two nights, and these only, the fishing was good. On account of this scarcity of cod in their own particular haunts, the boats from Stamsund *Vœrs* had to go West to the Ure grounds. The temperature of the water there was 6°, and the hauls were for some days very good, *but the fish were all milters.* On going still farther to the banks west of Ure, where the water is deeper, Meisfjord found 7°; still farther west, at Balstad, and then at Sund, the sea continued to be very warm: 7° at 70 to 75 fathoms' depth was usual, and no fish were caught. At length a rising ground, *Skalle*, was reached, where at 45 fathoms a temperature of 5° was found. Here the fishing was all that could be desired, and the catch made by Meisfjord's boat this season yielded about 25*l.* to each of the crew.[1]

Another appeal for help made by the Inspector-General to the Government in 1889 succeeded in at last arousing some interest in the matter. A steamer was despatched in 1891 with forty-five thermometers and sundry other scientific instruments. The fishermen received thirty-three of the thermometers, and from the ship a series of observations of the temperature at different depths in certain fixed places was made from February 21 to April 13. The next year this was repeated from January 12 to March 28, but the temperature observations do not appear to have been combined with actual fishing, and, as a consequence, the results may probably not be such as to induce the Government or Parliament to continue the experiment. The results at which the thirty-three fishermen with their thermometers arrived have not been allowed to transpire; perhaps they are not worth the expense of publication; but it would be a great pity for a subject so important to miscarry through a first false step. In contradistinction to the negative results of the Government stand the conclusions of Meisfjord. He says that when the favourable temperature is very uniform over a large area, the shoals are more scattered than usual, and therefore more difficult to find; further, he adds that, although a temperature of 5° suits the cod better than any other, shoals of them may occasionally be found in water a degree either warmer or colder, and this he ascribes to the presence of crustaceous food, the very thing to make a cod's mouth water, should he ever feel a dryness in that organ.

*Fishing Operations* (*continued*).—To return to the fishermen at work. After the haul has been made and the fish disentangled, the nets are, as a rule, immediately spread again, but at intervals they are taken to land and dried, to prevent them rotting. In the beginning of the season the lines are brought ashore every day to be baited; but later on, when the days are longer, the same line is often re-set.

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[1] See note on next page.

Lines are distinguished as day-lines or night-lines, according to the time at which they are set. The day-line boats generally leave the shore a little later than the others, in order to give the crews of the night-line boats sufficient time to haul and re-set their gear before the others commence. The latter remain near their lines until they are drawn in the evening, or perhaps leave earlier if fish are plentiful. The net boats and night-line boats go out early in the morning, haul their gear, put either the same or fresh tackle down, and return with their

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[1] As an example of how a fisherman can combine 'practical working with scientific investigations,' I give below one of the tables Meisfjord has sent us. His least successful season has been chosen.

| Date, 1890 | | Place and depth | Temperatures at depths in fathoms | | | | | | Number of fish caught |
|---|---|---|---|---|---|---|---|---|---|
| Nets set | Hauled | | Surface | 40 | 50 | 60 | 70 | 90 | |
| Feb. 8 | Feb. 17 | 50 fathoms . . . . | <br>2° | 5°<br>4°·5 | 6°<br>5°·5 | | | | 172 |
| " 17 | " 18 | Vesterkaasa, 40–50 fathoms . | 2°<br>2° | 4°·5<br>4°·5 | 5°·5<br>5°·5 | | | | 480 |
| " 18 | " 19 | Same place and depth . . | 2° | 4°·5 | 5°·5 | | | | 313 |
| " 19 | " 20 | " " " . . | 2°<br>2° | 4°·5<br>5° | 5°·5<br>6° | | | | 109 |
| " 20 | " 22 | Flat bed, 40 fathoms . . | 2°<br>2°·25 | 5°<br>4°·5 | <br>5°·5 | | | | 512 |
| " 24 | " 28 | East, rising bed, 40–50 fathoms | <br>2°·25 | 4°·5<br>5° | <br>6°·5 | | | | 603 |
| " 28 | Mar. 3 | Near Vesterkaasa, 50 fathoms . | 2°·25<br>2° | 5°<br>3°·5 | 6°·5<br>4° | <br>5° | | | 67 |
| Mar. 3 | " 6 | East, 50 fathoms . . . | 2°<br>2° | 3°·5<br>3°·5 | 4°<br>4° | 5°<br>5° | | | 48 |
| " 6 | " 7 | Moved to another place, 50 fath. | 2°<br>2° | 3°·5<br>3°·5 | 4°<br>4° | 5°<br>5° | | | 37 |
| " 7 | " 8 | Again to another, 50 fathoms . | 2° | 3°·5<br>Temperature not taken | 4° | 5° | | | 82 |
| " 10 | " 13 | Straight off Stamsund, 50 fath. | 2°<br>2° | 3°·5 | 4°<br>3°·5 | 5°<br>4° | <br>4°·5 | <br>5°·5 | 354 |
| " 13 | " 15 | On the edge of the bank, 60–70 f. | 2°<br>2° | | 3°·5<br>3°·5 | 4°<br>4° | 4°·5 | 5°·5<br>5°·5 | 159 |
| " 17 | " 20 | Farther out, 70–90 fathoms . | 2°<br>1°·75 | | 3°·5<br>3°·5 | 4°<br>4° | 4°·5<br>4°·5 | 5°·5<br>5°·5 | 744 |
| " 20 | " 21 | Same place and depth . . | 1°·75 | | 3°·5 | 4° | 4°·5<br>5° | 5°·5 | 287 |
| " 21 | " 22 | A little more east, 70 fathoms . | | | | | 5°<br>5° | | 160 |
| " 24 | " 25 | Still farther east, 40–50 faths. . | | 4°<br>4° | 5°<br>5° | | | | 255 |
| " 25 | " 26 | Farther towards Flæsen, 40–50 f. | | 4°<br>4°·25 | 5°<br>5° | | | | 1,328 |
| " 26 | " 27 | Same place, 50 fathoms . . | | 4°·25<br>4°·25 | 5°<br>5° | | | | 1,012 |
| " 27 | " 28 | " " " . . | | 4°·25 | 5°<br>4° | | | | 212 |
| " 28 | " 29 | Farther out, 60–70 fathoms . | | | 4°<br>Temperature not taken | | 5° | | 384 |
| " 31 | April 1 | 50–60 fathoms . . . . | | | 4°·5<br>4°·5 | 5°<br>5° | | | 309 |
| April 1 | " 5 | " " . . . . . | | 4°<br>4° | 5°<br>5° | | | | 400 |
| " 8 | " 9 | 40–50 fathoms . . . . | | 4° | 5° | | | | 215 |

catch. The time at which they reach shore depends upon how far they have had to go out, and also, of course, upon the weather. If the fish are found in deep water, and consequently close to the edge of the bank, the boats from the *Værs* in West Lofoten have a longer distance to cover than those from East Lofoten. Some of the former may have to do upwards of ten miles before they reach the fishing ground, and this means that they are unable to return until the afternoon, but when the fish are in the shallow water, close to land, the day's work is over in a few hours.

A good catch for a net boat is three hundred to four hundred fish, and for a line boat two hundred; six hundred to eight hundred for the former, and four hundred for a line boat are very good, and above that rich. Loaded to the gunwale means 1,200 to 1,500 fish in a net boat, and 600 to 1,000 in a line boat. If the catch is too great to be taken on board—3,500 have been recorded in one haul—the rest of the fish are not disentangled from the net, but, net and fish, dropped again into the water to be fetched next day. Sometimes less successful boats assist in carrying the fish to shore, or if the distance is not far, the fish may be strung on a line and towed to land.

The cod is killed by an incision behind the gills, and after it has been split up, the liver and the roe are taken out and deposited in separate tubs, while the offal is thrown overboard. This is done, if circumstances permit, during the return journey from the fishing grounds, and on reaching the *Vær* the greater number of the fishermen sell their fish at once to buyers, either on trading ships or on land, principally to the proprietors and storekeepers of the respective *Værs*. Some of the men dry, at least part of, their catch by hanging the fish up on long spars resting on wooden sheers. In the course of three or four months they become sufficiently dry, and are then, for the most part, sent to Bergen whence they are exported as 'dried cod' (*Törfisk*) chiefly to Italy, Sweden, and Holland. The roe is salted in barrels, and the fishermen usually dispose of it before leaving Lofoten. The heads of the fish are sold to manufacturers of fish manure. The fish sold to the merchant ships and to the proprietors of the *Vær* are mostly split, salted, dried, and sold as *Klipfisk*, chiefly to Spain.

The proceeds of the fishermen's toil during the three months in Lofoten do not seem an excessive living wage, but it illustrates, at all events, how a frugal, sober, and industrious race can work—hard and perilous work it is too—and be content with little. The following table gives the average number of fish and gross earnings per man in the last ten years.

| Year | Number of fish | Kroner | £ | s. | d. |
|---|---|---|---|---|---|
| 1884 | 612 | 215 | 11 | 18 | 11 |
| 1885 | 1,000 | 209 | 11 | 12 | 3 |
| 1886 | 1,072 | 225 | 12 | 10 | 0 |
| 1887 | 1,070 | 163 | 9 | 1 | 3 |
| 1888 | 813 | 191 | 10 | 12 | 3 |
| 1889 | 572 | 195 | 10 | 16 | 8 |
| 1890 | 1,022 | 245 | 13 | 12 | 3 |
| 1891 | 693 | 220 | 12 | 5 | 0 |
| 1892 | 540 | 143 | 7 | 18 | 11 |
| 1893 | 1,012 | 225 | 12 | 10 | 0 |
| Yearly average | 840·6 | 203·1 | 11 | 5 | 10 |

From this must be deducted the expense necessary to cover wear and tear of gear and boats, cost of board and lodging and of bait. The average for these items amounts to 5*l.* 4*s.* 5*d.* per man, but in some years, like that of 1892, not a few of the men must have returned from Lofoten poorer than they went.

The annual yield of the Lofoten fishery (official district) for the last five years has been:—

| Year | Number of fish | Barrels of common cod-liver oil | Barrels of steam-prepared cod-liver oil |
|---|---|---|---|
| 1890 | 30,000,000 | 32,800 | 14,400 |
| 1891 | 21,050,000 | 12,700 | 15,700 |
| 1892 | 16,250,000 | 13,000 | 7,000 |
| 1893 | 27,000,000 | 17,700 | 16,000 |
| 1894 | 28,200,000 | 12,100 | 10,600 |
| Average | 24,500,000 | 17,660 | 12,740 |

## Romsdal Fisheries.

Of the two great spawning fisheries, that of the Romsdal is the second in importance, and its main features are so similar to those of the Lofoten fishery that it requires only a passing notice.

As at Lofoten, the codfish approach the Romsdal coast in the beginning of the year. They make their way from the sea to the spawning grounds by passing through three deep channels: Bredsundsdybet, to the south; Boddybet, in the centre; and Griphölen, to the north; and then they disperse all over the banks, extending from Cape Stadt, lat. 62°, to the mouth of the Trondhjemsfjord, lat. 64°. The fishery district is, for administrative purposes, divided into three parts: to the south Söndmöre, with the town of Aalesund; in the centre, Romsdalen proper, with the town of Molde; and to the north, Nordmöre, with Christiansund. Söndmöre is notable as the birthplace of the improved methods of preparing cod-liver oil, for it was in this district, on the island of Giske, that Peter Möller, in 1853,[1] put up the first factory where the steam process was employed. He soon afterwards removed to Lofoten, but the process he had introduced continued to develop at Romsdalen, till in 1890 there were no less than fifty-four steam factories established in that district.

The yield of the Romsdal fishery is considerably less than that of Lofoten, and the following table shows the average results for the last five years (1889-93):—

| — | Number of fish | Barrels of common cod-liver oil | Barrels of steam-prepared cod-liver oil |
|---|---|---|---|
| Nordmöre . | 2,086,000 | 2,078 | 812 |
| Romsdalen . | 970,000 | 1,095 | 292 |
| Söndmöre . | 4,906,000 | 2,822 | 4,860 |
| Total . | 7,962,000 | 5,995 | 5,964 |

Maximum and minimum yields were in the same period for the whole district:—

| — | Year | Maximum | Year | Minimum |
|---|---|---|---|---|
| Fish . . | 1892 | 10,700,000 | 1891 | 6,200,000 |
| Common oil . | 1892 | 5,570 barrels | 1891 | 3,878 barrels |
| Steam - prepared oil . | 1890 | 8,377 „ | 1889 | 4,922 „ |

## Finmark Fisheries.

These are divided into four kinds, according to the seasons at which they are carried on: from January to April there is the *Got* or spawning fishery, from April to June the *Lodde* fishery, from June to September the summer fishery, and during the remainder of the year the autumn fishery. In the first of these only codfish are taken; in the second chiefly cod, but also a few others; while in the third and fourth a great variety of fish are caught.

*The Got Fishery.*—In Finmarken as well as at the other parts of the coast of Norway the cod arrive in January to spawn, and leave again in April. They do not, however, come in such enormous shoals as are found at Lofoten, and the fishing is not of sufficient importance to attract men from a distance; indeed, even the local fishermen do not pursue it to any great extent.

*The Lodde Fishery.*—When the spawning cod have left, the caplin, or *Lodde*, appear in such enormous numbers that they may, sometimes, envelope the coast for fifty or a hundred miles, at the same time extending from the shore for many miles out to sea, and so closely packed together that they can be ladled out of the water with a scoop.

This of course is a grand opportunity for the larger fish, as the *Lodde* is small and easily swallowed. Consequently in its wake come shoals of cod, sometimes almost equal to those at Lofoten. These at first have the *Lodde* all to themselves, except for the whales and seagulls; but a little later the haddock puts in an appearance, and towards the close of the caplin's stay, coal-fish in great numbers together with torsk, plaice, halibut, wolf-fish, and many others join the feast.

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[1] In an earlier work the writer has named the year 1850 as being the first in which Peter Möller introduced his process; but as the next year or so was taken up in preliminary experimental work, and the manufacture on a commercial scale not actually commenced till 1853, the latter date is, perhaps, more correct.

The *Lodde* are very irregular in their habits. The great body of them, as a rule, arrive in April and remain to the end of May, but there are many exceptions to this. Sometimes they come as early as December, at other times not before May, and indeed they may not appear at all for years, as was the case from 1830 to 1845.

Further they are just as uncertain in respect to the places they frequent. Sometimes they go to East Finmarken, while in other years West Finmarken has the benefit of their visit. Sometimes they keep quite close to land, at other times they remain in deep water, or are constantly shifting about from place to place. Their friends, including the cod and the cod fishermen, of course do their best to follow all these erratic movements, but nevertheless the *Lodde* fishery is very much like a game of chance—sometimes turning out very profitable to those who pursue it, and in other seasons resulting in nothing but labour lost.

Despite this uncertainty the Finmark fishery stands very high in the esteem of the fishermen. In fact it seems as if the uncertainty was in itself the main source of attraction, and, after all, this is by no means surprising. The majority of mankind are strongly susceptible to the fascinations of the uncertain, as may be seen in the way they conduct not only their pastimes, but also the serious business of life. To this rule the Norwegian fisherman is no exception, as in one way, at least, is shown by his hankering after the fishing lottery at Finmarken. To take part in this he will sacrifice an absolute certainty elsewhere, and at Lofoten we find that it is impossible to induce the men to remain after the arrival of the usual reports of big catches of fish at the opening of the season in Finmarken. The fishing at Lofoten may still remain most productive; indeed, towards the end it is often at its best; and the catches in quantity and quality should satisfy, and even more than satisfy, the fishermen. This, however, has no effect, and, no matter how good the fishery may be, the men will not stay, but away they go to try their fortune at Finmarken.

They make the journey in the large boats —the *Femböringer*—and in these they live throughout the fishing, as the accommodation on land is very insufficient. The boats are fitted with a removable deck in the aft-part, and under this the crews manage to find some shelter and rest.

From ten to twenty thousand fishermen are present in the season, of whom only about four thousand are local men, and the great majority of the rest come directly from the Lofoten fishery. The tackle used is the handline and the longline, both being baited with caplin. The handline is particularly easy to work here because the fish are often found close to land, and at a depth of only two or three fathoms. On the other hand, when they happen to keep far out and in deep water it is no easy task to haul the heavy cod to the surface. Then also there is a difficulty in regard to bait, for when the caplin remain, say, one or two hundred fathoms down it is impossible to get at them, and herrings sent from other districts have to be used as bait. Some experiments devised to keep the caplin fresh by freezing have been made lately, but so far as the writer is aware these have not been practically successful.

The cod that appear with the caplin are not the same as those which visited the coast in the earlier month of the year for the purpose of spawning. A few indeed may show signs of having recently spawned, but the bulk consists of younger fish not yet ripe for spawning. They are therefore somewhat smaller than the Lofoten cod, and when split they weigh, according to Capt. Juel, from two to a little over six pounds, whereas in Lofoten the fish are scarcely ever under five pounds, and in some of the *Værs* they occasionally average as much as eleven pounds. The Finmark fish are distinguished from those of Lofoten by the name *Lodde-torsk* (caplin-cod): it is from this that the name of the fishery—*Lodde* fishery—is derived, and not, as might be supposed, from the caplin directly.

The annual yield of the *Lodde* fishery for the last five years has been :—

| Year | Number of fish | Barrels of common liver oil | Barrels of steam-prepared liver oil |
|---|---|---|---|
| 1890 | 13,652,000 | 19,740 | 1,209 |
| 1891 | 11,868,000 | 15,120 | 667 |
| 1892 | 20,000,000 | 28,056 | 3,367 |
| 1893 | 12,776,000 | 18,156 | 1,793 |
| 1894 | 16,322,000 | 16,575 | 4,730 |
| Average | 14,923,000 | 19,530 | 2,351 |

*Summer and Autumn Fishery.*—As a rule the caplin finish spawning at the end of May, and then suddenly disappear, together with the great bulk of the codfish. Still a few of the latter remain and also large numbers of haddock, coal-fish, and torsk. These feed upon the roe left behind by the caplin, and, later, on the fry. The fishing is therefore still continued, and for some time it gives employment to a considerable number of men besides those who live in Finmarken. Soon, however, the outsiders have to return home to attend to the spring work on the little plots of land which they possess and cultivate. About five or six thousand of those who do not live too far away, generally return to Finmarken after having finished their farm work, and take part in the summer fishery. At the end of July they have again to go home for the hay harvest, which in those latitudes occurs about that time.

Nearly eleven thousand men are employed in the summer fishery, and the catches then obtained consist chiefly of coal-fish.

The produce of the summer and autumn fishing averaged annually, during the quinquennials 1881–1885, 13,986; and 1886–1890, 9,850 barrels of all sorts of liver oils.

# COD-LIVER OIL

Although we have no record fixing the exact date when cod-liver oil was first used, yet we know that it is a remedy of very respectable age. The Greenlanders, Laplanders, and Esquimaux were acquainted with its virtues long before they came in touch with civilisation, and during the palæolithic stage of their existence. The oil used by these primitive peoples was doubtless a very crude product, and the earliest improvement in its preparation with which we are acquainted was dependent upon the introduction of iron vessels. By using these the application of heat was rendered possible, and a much larger quantity of oil was expressed from the livers. This, however, was only a quantitative improvement, and it is very remarkable that, although many centuries have since elapsed, the method of preparing cod-liver oil remained exactly the same, and not a single step was taken towards improving its quality until the year 1853, when Peter Möller invented and introduced that great advance upon the older method—the steam process of extraction.

*The Liver.*—Before entering upon the details of the modern methods of preparing cod-liver oil, it will be well to give a brief description of the source of the oil—the liver of the cod-fish. In size the livers vary considerably, but their average weight may be stated at a little over half a pound,[1] as, taking one year with another, a hectolitre contains about four hundred livers, weighing about 220 lb. A liver of that weight, with its flaps extended, is about 14 inches in

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[1] The following figures are taken from our own statistical tables. The first four columns state the number of livers from net- and line-fish required to fill a hectolitre on the first and on the last day of each year's season. The other columns show the averages from both varieties of fishing at the beginning, the end, and throughout the whole season respectively:—

| Year | At the beginning of the fishery | | At the close of the fishery | | Average at the beginning | Average at the close | Average for the whole season |
|---|---|---|---|---|---|---|---|
| | Line-fish | Net-fish | Line-fish | Net-fish | | | |
| 1885 | 450 | 350 | 935 | 630 | 400 | 780 | 590 |
| 1886 | 410 | 320 | 650 | 500 | 365 | 575 | 470 |
| 1887 | 450 | 412 | 750 | 580 | 430 | 665 | 550 |
| 1888 | 315 | 285 | 450 | 395 | 300 | 420 | 360 |
| 1889 | 275 | 260 | 550 | 400 | 270 | 475 | 370 |
| 1890 | 300 | 245 | 560 | 400 | 280 | 480 | 380 |
| 1891 | 395 | 300 | 530 | 378 | 350 | 455 | 400 |
| 1892 | 410 | 300 | 500 | 450 | 355 | 475 | 415 |
| 1893 | 380 | 285 | 540 | 410 | 330 | 425 | 380 |
| 1894 | 500 | 420 | 900 | 625 | 460 | 762 | 611 |
| Average | 389 | 318 | 637 | 477 | 354 | 551 | 452 |

The last column shows an average for the ten years of 452 livers to the hectolitre, but this is only approximately correct. The averages are based upon the first four columns, and presuppose an equal number of livers from line-fish and net-fish, thus giving a figure that is a little too high. The writer's experience leads him to think that about 400 comes nearer the mark; but of course there are great variations, as in 1883, when as many as 1,800 livers were required to fill the hectolitre. Net-fish, it will be seen, give larger livers than line-fish, and the livers of both are fatter at the beginning than at the end of the season.

length and about 2½ inches thick at the central part. This is the general size, but in years, like 1883, when the fish are exceedingly lean, a great number of their livers weigh less than 2 oz. each On the other hand, livers of much larger size are obtained sometimes. The biggest that ever came under our notice was 43 inches long, 6½ inches thick, and weighed over eleven pounds.

The liver of the cod-fish, when healthy and fat, is cream-coloured, and so soft that the finger may be pushed right through it without any effort. The leaner the liver, the tougher it is, and its colour deepens to a reddish or even to a nearly black hue. There are always a certain number of diseased livers to be found amongst the healthy ones. These are recognisable by the presence of coloured spots, or by their being wholly or partly of a green colour. Such livers ought never to be employed for making medicinal oil; but manufacturers who compete for cheapness cannot well afford to reject them, as their percentage is such as to form a considerable item in the manufacturing account.

Like those who are somewhat higher up in the scale of life, the cod-fish has its seasons of prosperity and adversity. In some years they flourish and thrive and produce livers that are real beauties, in others they seem to fall upon evil times, and then their livers are of the lean and ill-favoured variety. ‘Seven bountiful and seven barren years’ is one of the many time-honoured sayings which stand high in the fishermen's estimation. It expresses the idea well enough in a general way, but, like other popular sayings which have the misfortune to condescend upon anything so precise as numbers, it is distinguished by its disagreement with dry facts, as may be seen from the preceding tables.

The result of this great diversity in the quality of the livers obtained in different years is, that at the beginning of each season there is no certainty as to what will happen. This, of course, is very welcome to the speculator, who is always ready to create a panic by holding forth the dread of poor livers. An amusing but by no means inaccurate description of the *modus operandi* of these speculators was given in the *Chemist and Druggist* of March 3, 1894, from which we may quote the following: —after some extracts from circulars issued by dealers anxious to dispose of their stock—*e.g.* ‘the reports from Lofoten are very discouraging’; ‘stormy weather is still prevailing on the grounds and fish are scarce’; ‘prices have risen considerably during the last fortnight, and a further rise must be expected’—the journal goes on to give the following sound advice: ‘Buyers should remember that year after year the curtain of the cod-fishing melodrama rises on the horrible entrance of the lean-livered spectre set off by a weird background of elementic wrath only to fall on the apotheosis of the prosperous speculator surrounded by the accumulated gains of a prolific oil harvest.’ In the previous year (1893) the production of steam-prepared oil had reached the unprecedented figure of 29,254 barrels, a large percentage of which must have been in the hands of speculators at the beginning of 1894, at the very time when they commenced to work their lamentations. Further, of course, it should be remembered that, whenever there is a deficiency in the Lofoten produce of oil, Finmarken is ready to fill the gap, as corroborated by the statistical tables already given.

*Methods of preparing Cod-liver Oil in Norway.*—The primitive method, which is still used to a certain extent, is as follows. As soon as the fishermen reach the *Vær*, and finish separating the livers and roes, they sell the fish and carry the livers and roes up to their dwellings. In front of these are ranged a number of empty barrels into which the livers and roes are placed, separately of course. The fishermen do not trouble to separate the gall-bladder from the liver, but simply stow away the proceeds of each day's fishing, and repeat the process every time they return from sea, until a barrel is full, when it is headed up and a fresh one commenced. This is continued up to the end of the season, when the men return home, taking with them the barrels that they have filled. The first of these, it may be noted, date from January, and the last from the beginning of April, and as on their arrival at their homes the fishermen have many things to arrange and settle, they seldom find time to open their liver barrels before the month of May. By this time the livers are, of course, in an advanced stage of putrefaction. The process of disintegration results in the bursting of the walls of the hepatic cells and the escape of a certain proportion of the oil. This rises to the top, and is drawn off.

Provided that not more than two or three weeks have elapsed from the closing of the barrel in Lofoten to its being opened, and if during that time the weather has not been too mild, the oil is of a light yellow colour, and is termed raw medicinal oil (Norw. *Raa Medicin Tran*). As may be supposed, however, very little oil of this quality is obtained. Indeed, as a rule there is so little of it that the fishermen do not take the trouble to collect it separately. Nearly all the barrels yield an oil of a more or less deep yellow to brownish colour: this is drawn off, and the livers are left to undergo further putrefaction. When a sufficient quantity of oil has again risen to the surface, the skimming is repeated, and this process is continued until the oil becomes a certain shade of brown. The product collected up to this point is known as pale oil (Norw. *Blank Tran*). By this time the month of June has generally been reached, and with the warmer weather the putrefaction is considerably accelerated, and the oil now drawn off is of a dark brown colour, and is collected by itself. It is rather misleadingly called light brown oil (Norw. *Brun Blank Tran*). When no more can be squeezed out, the remainder is thrown into an iron caldron and heated over an open fire. By this process the last rests of oil are extracted from the hepatic tissues, which float about in the oil like hard resinous masses, termed *Graxe*, and used as manure. In order to fully carry out the extraction, it is necessary to raise the temperature considerably above the boiling point of water. This is well shown by a simple test frequently employed by the fishermen who, in order to ascertain if the requisite heat has been attained, squirt a small quantity of water into the oil, and if it has reached the proper temperature the water is instantaneously converted into gas with an explosive-like noise. The oil prepared in this way is very dark, almost black, and with a greenish fluorescence in reflected light. In thin layers and by transmitted light it shows a brown colour, and it is therefore termed brown oil (Norw. *Brun Tran*).

Not all the fishermen, however, prepare the oil themselves. Most of them, in fact, are compelled to sell the livers to the shop or store keepers, who supply them with such goods as they and their families require. The reason for this is the system of credit which in these regions has developed almost into a science. The method works somewhat as follows. The local storekeeper supplies the fisherman with whatever he wants, and he in return undertakes to deliver all the proceeds brought back by him from Lofoten the next year. The storekeeper, again, is also supplied on credit by a merchant at Bergen, and on exactly similar conditions. He must bind himself to send to the merchant all he has to sell, and he is not allowed to stipulate any price for his goods. The prices are determined by the merchants of Bergen, who are the real controllers of all this credit system. They meet together at intervals and fix the prices to be paid for the produce received, having proper regard to the state of the market and, of course, an eye to their own profit.

This system works so beautifully that the fisherman who has once got into the grip of the storekeeper can seldom emancipate himself, nor can the storekeeper in his turn free himself from the control of the merchant. Many of the storekeepers suffer from what may be called chronic intermittent bankruptcy. They are continually failing, and by each failure the merchant is apparently a great loser. Curiously enough, he is always ready to give the storekeeper credit again. As this process goes on for generations, one cannot help thinking that somehow it must be a paying business for the merchant, whatever it is to the others concerned.

In this way the storekeepers are enabled to collect the cod livers from great numbers of the fishermen, and as a consequence they supply by far the largest amount of the raw medicinal oil which comes into the market. The storekeepers and fishermen send almost all their products to Bergen, which is, therefore, the great emporium for cod-liver oil, but none is *manufactured* there. When the oils reach Bergen they are set aside for a time in order to allow water and impurities to settle. When this has been completed the oil is drawn off, and such as happens to be deficient in the properties qualifying it for one of the four classes above mentioned is boiled, mixed, and manipulated until it has acquired those properties. Sworn sorters, who are appointed by the city of Bergen, may be called in to decide disputes as to the quality of an oil. They are not bothered with any scientific knowledge, but simply carry out their analysis of an oil by dipping the finger therein, conducting it to the olfactory test organ, and thence, to the gustatory ditto. This, in their opinion, is the alpha and omega of a careful and exhaustive analysis, which being made, they proceed to pronounce judgment. As long as they keep within the legitimate limits of knowledge gained by actual experience, their decisions may be fair enough. Sometimes, however, they affect to understand more than any experience of this sort can teach, and then the decisions they give pass from the useful to the ridiculous.

Up to the year 1853 the supply of cod-liver oil was dependent upon the methods above stated. The late Peter Möller was intimately acquainted with the primitive methods of making the oil; for many of his younger days had been passed at the fishing places, and in addition he was an enthusiastic student of chemistry, so that perhaps there was nothing very wonderful in his conceiving the idea of how the manufacture of cod-liver oil might be improved. After his method had been made known he was publicly told that 'anybody might have done that,' which, of course, was perfectly true, only nobody did it. Cod-liver oil had been made for centuries, and yet it never seemed to occur to any one of the hundreds of manufacturers that there was an opening for improvement; and, *pace* those who knew all about it after they had been told, if it had not been for Peter Möller the older methods might have been the only ones up to this present day.

But, whatever praise may be due to him for the merits of his invention, his chief claims lie rather in the energy and tenacity of purpose that carried his ideas through the greatest difficulties to universal recognition and appreciation, and for the entire unselfishness of his aims. He not only disdained to secure patent rights for his invention, but he freely communicated all the details of his process, and did all that was possible to make his ideas widely known. Indeed, he actually went further, and endeavoured to encourage and persuade others to adopt and profit by the new method of manufacture; and one of his first acts after perfecting his apparatus was to give away two complete sets—one to Christiansund and the other to Storvaagen in Lofoten.

The usual consequences followed. The other manufacturers of cod-liver oil took up an attitude which at its best might be described as armed neutrality, and to this they stuck so long as Peter Möller was struggling to bring his new process into practical use, and to open up a market for its produce, which at first was no easy matter. The buyers, accustomed to the brown oils prepared from putrefied livers, *actually refused to believe that the colourless and* *almost odourless and tasteless product of the new method could be cod-liver oil at all.* It was only with great difficulty that they were convinced; but when at length it came to be understood that the oil really could be made by a process hitherto undreamt of, and made without the undesirable qualities which for centuries had been supposed to be necessary—because irremovable—evils, then the whole scene changed. The demand for the new oil became enormous, and the inventor had the satisfaction of seeing those who had stood aloof when he was bearing the brunt of the battle now humbly doing their best to follow in his wake. Factory after factory was established for the purpose of carrying out his method, and at the present day there is scarcely a nook or corner on the whole Norwegian coast in which one is not to be found.[1]

In 1853, the first year in which the colourless oil was practically made, the total quantity produced was twenty barrels, and even this small supply was obtained only with the greatest difficulty. It was essential to have the livers in a fresh condition, and, strange as it may seem, such livers were then hardly to be procured. The great majority of the fishermen were unable to sell any of their produce, as they were bound by the pernicious credit system to hand it all over directly to the storekeepers. The men who were not in the hands of the storekeepers were too conservative to be easily induced to change their customs. Putrid livers had hitherto seemed to them all that anyone could possibly desire, and not even the offer of temptingly high prices could persuade them to supply fresh livers. Peter Möller was not, however, the kind of man to be baffled by a difficulty such as this. He had already overcome many and much more formidable obstacles, and just as an instance of his determination and energy we may mention that, although he was then a man on the wrong side of sixty, he spent several weeks of the coldest and stormiest part of 1855 sailing in an open boat on the arctic seas in order that he might personally supervise and carry out his plans.

Now, all is changed. No one cared to buy any of the original twenty barrels of oil, but at the present day hardly any other kind is in demand, and the production has increased from the twenty barrels of 1853 to an annual output approaching thirty thousand barrels in Norway alone.[1] Even the fishermen have been taught by experience. They are now eager to sell the livers fresh, and the higher prices which they thus obtain for their produce are helping in a large measure to make them independent of their *bête noire*, the storekeeper. Such, in a few words, is the forty years' history of 'a great industry which has been built up in these northern regions,' to quote a recent writer upon this subject.

The new method of preparing cod-liver oil which Peter Möller devised and introduced is, like most inventions, a very simple matter—after it has been invented. It is now generally known as the 'steam process,' and *the essential difference between it and the older methods is that the oil pure and simple is extracted from the livers instead of the oil mixed with a great*

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[1] The following table shows the increase of these factories since 1870, nearly twenty years after the new process was first established:—

| Year | 1870 | 1875 | 1880 | 1885 | 1890 |
|---|---|---|---|---|---|
| Number of factories | 57 | 73 | 75 | 117 | 148 |

The above figures do not, however, give a proper idea of either the number or development of the factories, as they do not include factories on board ships, which are certainly very numerous.

[1] The production in the last six years has been in barrels (=231·5 lb. = 25·5 gallons, or 1·158 hectolitre at 15° C.)—

| — | 1889 | 1890 | 1891 | 1892 | 1893 | 1894 |
|---|---|---|---|---|---|---|
| Finmarken | 3,685 | 1,209 | 667 | 3,367 | 1,793 | 4,730 |
| Tromsö County | 484 | 192 | 86 | 1,217 | 2,024 | 1,500 |
| Nordland County: | | | | | | |
| Lofoten | 11,140 | 14,421 | 15,717 | 6,995 | 16,063 | 10,622 |
| Ydersiden | 1,500 | 1,541 | 870 | 911 | 3,942 | 2,184 |
| Rest of the county | 27 | | 20 | | 82 | ? |
| Northern Trondhjem County | | | | | 212 | ? |
| Nordmöre | 1,036 | 691 | 605 | 1,036 | 691 | 864 |
| Romsdalen | | 432 | 302 | 302 | 130 | 302 |
| Söndmöre | 3,886 | 7,254 | 4,262 | 4,577 | 4,317 | 860 |
| Total | 21,758 | 25,740 | 22,529 | 18,405 | 29,254 | 21,062 |

*number of decomposition products.* It was these decomposition products that gave the oil what was supposed to be its characteristic brown colour and far from delightful smell and taste. They were derived from the putrefaction of the albuminous constituents of the liver, and it was very natural that they should be supposed to be part and parcel of the oil when that was obtained by leaving the livers until, by putrescence, the hepatic cells were broken up, and the oil globules in them allowed to exude.

The introduction of the steam process, however, showed that these products of putrefaction were not an essential constituent of cod-liver oil from the chemical point of view; and from the therapeutical, subsequent experience has shown that they have nothing to do with the beneficial action of the oil, if indeed they do not detract from it. This last is a point on which the writer would rather not express an opinion, as brown oils are actually used to a certain extent for medicinal purposes at the present day; but he would ask if, apart from colour, taste, and smell, it is a desirable thing, indiscriminately, to add the ptomaïnes produced by the putrefaction of albumen, to any medicinal remedy whatsoever.

When, therefore, the steam process is carried out with proper regard to its essential principle, the livers must be used absolutely fresh; indeed, if over twelve hours are allowed to elapse after the capture of the fish, no first-rate oil can be produced from their livers. As soon as the livers are landed, they should be carefully sorted, and all poor, small, bruised, and diseased specimens thrown aside. Those finally selected should be thoroughly cleansed from blood, membrane, and other impurities by washing in several waters; and, then, after the gall-bladder has been severed, they should without delay be deposited into the melting-vessels.

There are three different ways by which the melting operation can be carried out. The original method adopted by Peter Möller was to heat the livers upon a water-bath of large dimensions. The apparatus required for this is now manufactured wholesale in Norway. It is made of tinned iron sheets, and may be purchased for less than 10*l.*; a price that places it within the reach of everyone, and that to a large extent explains its almost universal use.

Another form of the apparatus consists of double-walled vessels, or jacketed caldrons, which are heated by conducting a current of steam between the external and internal walls. Each vessel is provided with a self-acting regulator by which the pressure of the steam is controlled to a nicety, and inside each there is a stirring apparatus worked by steam power. This is the form of apparatus that we ourselves employed until two years ago.

The third variety is an adaptation for use on board vessels. The liver-receiver is made of wood, in the shape of a truncated cone, with the larger end forming the bottom, the smaller one the mouth, and the steam from a small separate generator is conducted directly into the livers. It is favoured by some makers of the oil because the vessels are able to move from one place to another, dropping anchor wherever there is a prospect of a good supply of liver; but the ordinary apparatus cannot be employed, as even in the most secure of the harbours there is, at times, too much rolling. Also because it makes the manufacturer independent of the proprietors of the *Vœrs*, who sometimes exact a pretty high rent for permission to erect factories on their ground. The factories on board ship are fairly numerous, but, apart from those referred to, they have no advantages over the factories on land. We have seen it stated that by this method the oil is prepared from fresher livers, because the melting process is performed on board a vessel that can follow the fishermen, and so secure the liver in a fresher condition than the factories on land. That this is impossible should be evident from the description already given of the fishery; the livers cannot be obtained before they are detached from the fish, and this is done by the fishermen as they are returning from the fishing grounds, and is never completed before the *Vœr* is reached; the livers are then at once sold, and the factories on *terra firma* have quite as good a chance of getting the liver fresh as those afloat. The practice is for each factory to have its own regular set of suppliers from amongst the boats. Besides, the practical collection and preparation of livers in the open sea are too ridiculous to be believed by any except the innocent landsmen.

In all the three kinds of apparatus the process of preparing the oil is based upon the same principle—to force the oil out of the hepatic cells by a moderate heat and in a short time.

It is, of course, somewhat difficult to state the minimum length of time which manufacturers allow for heating the livers, but from hearsay and personal knowledge we believe that it is generally from two and a half to three hours. Of late, however, the oil has been sold so cheaply that we cannot help thinking that the livers are being heated for a much longer time, in order to increase the quantity of oil extracted from them. When the livers have been exposed to this heating process for such a length of time as the manufacturer thinks most profitable, the oil is drawn off and filled into barrels. The remainder, a thick pulpy mass, is known as *Graxe*, the liver-rests. By some it is put into bags and pressed, but so quickly does putrefaction ensue, that the oil obtained in this way is dark, in colour similar to the light brown or brown oils, and possesses a very rank, unpleasant odour, which is increased with the least delay in the pressing operation. Some manufacturers, therefore, simply shoot the pulpy mass into the sea without attempting to get more out of it, even though the oil it contains amount to 9–10 per cent. of the original weight of the livers. When the liver-rests are pressed and the oil is extracted there remains a dry, compressed mass which is generally either thrown away or sold to fish-guano manufacturers. Even this contains oil to the amount of 25 per cent. of its own weight; but that oil cannot be obtained by mechanical means, and its extraction by other methods would be too expensive to be profitable.

In the first variety of apparatus mentioned above, the temperature cannot, of course, rise above the boiling point of water, so that there is no possibility of regulating it beyond that. In the second apparatus any desired temperature may be reached and maintained up to some degrees above 100° C. In the third the livers come in direct contact with superheated steam, which is more or less above 100° C.

In respect to the quantity of oil produced by the three forms of the steam apparatus, the second may be made to yield most,[1] whilst the third gives the poorest result; but in their rapidity of working the third takes the premier position, while the first variety is the slowest.

In regard to the quality of the oil they produce there arises the question, What is understood by a first-rate oil? This is a very comprehensive term, as the writer has had frequent opportunities of observing. Leaving adulterations out of the question, and assuming a

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[1] The oil which we make for sale in barrels (as distinguished from the bottled oil) is prepared in the same way as all the other oil branded 'Finest steam-prepared Lofoten (or Norwegian) Cod-liver Oil,' and, therefore, the following table, taken from our own statistics, may be accepted as showing the percentage of oil yielded by the liver. The table gives our results from the year 1883, which was exceptionally poor, and it shows that with the exception of a single year, 1884, the livers contained a considerably larger proportion of fat at the beginning of the season than towards the end.

| Year | Average: first half of season | Average: last half of season | Average: whole season |
|---|---|---|---|
| | Per cent. | Per cent. | Per cent. |
| 1883 | 23·2 | 19·8 | 20·0 |
| 1884 | 43·0 | 47·0 | 46·6 |
| 1885 | 50·0 | 42·0 | 45·5 |
| 1886 | 53·0 | 48·0 | 49·0 |
| 1887 | 46·0 | 40·0 | 43·5 |
| 1888 | 54·0 | 51·0 | 53·0 |
| 1889 | 54·0 | 51·0 | 52·9 |
| 1890 | 58·0 | 55·5 | 57·5 |
| 1891 | 57·6 | 54·5 | 56·1 |
| 1892 | 55·8 | 54·7 | 55·7 |
| 1893 | 57·6 | 55·2 | 55·4 |
| 1894 | 47·1 | 41·3 | 44·3 |

genuine specimen of oil from *Gadus morrhua*, no chemical test was known by which its good or bad qualities could be determined.

Colour, taste, and smell are therefore the only criteria by which an oil is judged. By many, freedom from the so-called stearin is considered an important quality in a first-rate oil ; but this is a questionable virtue, as will be shown hereafter; and, besides, the removal of stearin is a subsequent operation, so that its presence or absence has nothing to do with the manufacture of the oil. In respect to colour, taste, and smell all the three varieties of the apparatus when properly used are capable of giving equally good results.

This, however, is by no means the whole matter, for in addition to the colour, taste, and smell of the oil it has another quality hitherto quite neglected by everybody concerned except the consumers. They also would no doubt be very glad to neglect this quality, but unfortunately for them it is far too much in evidence to permit of that being done. When the cod-liver oil has reached the stomach, it sets up, particularly in delicate constitutions, a series of proceedings known as eructations, or 'repeatings.' These are far from being pleasant to the patient, and after he has taken the oil for some time, and knows from his unhappy experience the horrors that will certainly follow each dose, he acquires an unspeakable disgust at the remedy. He may indeed force himself to persevere, or he may perhaps be compelled to do so by various forms of persuasion, but in either case, and especially in sensitive, delicate patients, it becomes doubtful in the circumstances if the game is worth the candle. That cod-liver oil should have such a drawback was obviously a matter very much to be regretted, if not indeed to be ashamed of, in these days of progress. This, at all events, was the view we took of the matter, and it also suggested the long series of practical and scientific experiments which we have carried out. These experiments have taught us many things concerning cod-liver oil and bodies allied to it which are of no little scientific interest, and which, in addition, are of at least some practical importance. As our knowledge of the properties of fats in general, and of cod-liver oil in particular, was in this way increased, we were gradually led to a more correct understanding of the nature of cod-liver oil from the chemical point of view, which in its turn was the means of explaining the peculiar physiological action of the oil and its special value from the therapeutical aspect. But this is by no means all, for in addition to these more or less academic results our investigations also led us to a practical result which is not only of theoretical interest but of real importance. This will be described in the section dealing with the new methods of manufacturing cod-liver oil which we have now introduced at Lofoten.

*Cod-liver Oil from other Countries.*—Amongst the cod-liver-oil-producing countries Norway is *primus inter pares*. It is due in part to the fact that the Norwegian fisheries are carried on under conditions which are much more favourable than any to be met with elsewhere. This alone was sufficient to give Norway the first place, but the introduction of Möller's process gave her another advantage. It effected a complete revolution in the methods of preparing the oil, and of course Norway had the lead in the new departure. The improvement in cod-liver oil that was effected by Möller's steam process, and the consequent very marked increase in the consumption of the oil itself, gave a great impetus to the industry; moreover, it so happened that Norway was the very place, we might say the *one* place, where the new process could be carried out to perfection on a sufficiently large scale. Indeed, the conditions with which nature has endowed that country seem as if they had been specially designed to meet the requirements of Möller's invention.

The consequence of this was that when the new process had been introduced, and had supplanted, practically, all the older methods of making the oil for medicinal purposes, the advantages already possessed by the Norwegians over their rivals were enormously increased.

The steam process, as we have said, requires absolutely fresh materials, and while these can be obtained with ease in Norway they, on the other hand, can be obtained only with difficulty, if indeed at all, elsewhere. The fishing grounds at Lofoten and Romsdalen are situated so near the coast that the boats leaving the *Vœrs* in the morning are back again with their catch of fish in the course of a few hours. This makes it quite easy to dispose of the livers before any decomposition whatever has set in. A second advantage possessed by these northern regions is their low temperature; during the whole of the fishing season at Lofoten the temperature is close to the freezing point. In the fisheries carried on in places or seasons where the prevailing temperature is bound to be much higher, the lapse of only two or three hours, or the exposure of the livers to the rays of the sun for even a shorter time, would be more than sufficient to destroy them; and therefore supposing they could be brought ashore elsewhere, as quickly as at Lofoten and Romsdalen, still no first-rate oil would be obtained from them. A third advantage of the Norwegian fisheries is the large supply of raw material available. It is quite impossible to carry on a steam factory unless an abundant supply of livers can be constantly obtained, and this of course is possible only at fishing centres to which a great number of boats resort, as is the case in the *Vœrs* of Lofoten and Romsdalen.

These are the three conditions which are absolutely necessary for carrying out the steam process of preparing cod-liver oil. Where even one happens to be absent the successful manufacture of the oil becomes very difficult if not altogether impracticable, and we may add that, so far as we are yet aware, with the single exception of Norway, these three essential conditions will hardly be found existing together in one and the same place. We ourselves have carried out a special and detailed investigation of the capabilities of most of the European districts where cod fisheries of any importance are to be found, and in all we have been met by the same insurmountable difficulty—the absence of one of these three conditions without which the first-class oil cannot be produced.

*Iceland.*—According to the reports furnished to us by Mr. Heyerdahl, who visited the country for the express purpose of carefully investigating its capabilities for the production of cod-liver oil, the fisheries of Iceland are, on the whole, very similar to those of Norway—with the exception of one condition. This is the third of our three essentials—the supply of a sufficient quantity of fresh livers to keep a steam factory going. Of course the total quantity of cod liver obtained in Iceland would be sufficient to supply a large number of factories, but unfortunately it cannot be utilised because it cannot be brought together at any one point in sufficient quantity while it is yet fresh. In the case of a steam factory where Möller's process is properly carried out the available supply of liver is just that supply which can be collected in an absolutely fresh condition; and as it seems practically impossible to obtain such a supply anywhere in Iceland it follows that we cannot expect that country to produce any steam-prepared cod-liver oil of the best quality.

Some years ago an English company erected a factory at Njardvik, in Iceland, but in a very short time it was abandoned. This was a practical demonstration of the correctness of the conclusion at which we had already arrived, for the factory had to be given up simply because a sufficient supply of fresh raw material, at paying prices, could not by any means be got together. The reason for this is to be found in the conditions under which the fishermen in Iceland live. In addition to their occupation as fishermen they are, almost without exception, also farmers. The plots of land which they cultivate are situated up country, and when the fishing season arrives, they come down to the fjords, but do not congregate at any special centre as in Norway; their fishing huts are scattered all over the shores of the fjords, and each man conducts operations from *his* house; from this he sails out and catches whatever fortune happens to 'bring to the net,' with this he returns to *his* house, and if anyone wishes to have the livers from the fish caught they must go to him for them; it becomes therefore a practical impossibility to secure fresh livers in any reasonable quantity. The better kinds of even the common oils are not produced by the Icelanders, but only the brown oil—exactly the same as that made by their forefathers in the year 1000 or thereabouts. They are not a people who take kindly to modern ideas, and they resent the advice of outsiders, however well meant it may be, and this not only in regard to the way of making cod-liver oil.

*North America.*—The writer has no personal knowledge of the fisheries of the United States, Canada, or Newfoundland, and has not been able to find any reliable literature sufficiently exhaustive to give a proper idea of the cod-liver-oil industry in those countries. There are a few steam factories working at some of the seaside towns of Massachusetts and Maine, but their products cannot bear comparison with the best Norwegian oils—so far as can be judged from what has been found at various exhibitions. The bank fisheries of America, being conducted far from land, and in the hot summer months, cannot supply the fresh livers required for steam-prepared oil. The off-shore fishery, however, occurs in winter, when the spawning fish visit the coast, and should furnish proper raw material for an irreproachable oil. Why it does not is not apparent to outsiders.

*British Isles.*—The production of the best variety of oil in England is not practicable except in very small quantities, and on relatively rare occasions. Nearly all the cod-fish are sold fresh for immediate consumption, and as the livers are disposed of together with the fish they are not available for making cod-liver oil. Further the chief fisheries are on the banks in the North Sea, and therefore too far from land, and the winters are, as a rule, too mild for the proper working of the steam process, even were it possible to obtain a supply of material from the off-shore fishery.

*Russia.*—There is only one other place in Europe where cod-liver oil is prepared—that is, Russia—on the seaboard stretching from the Norwegian boundary towards the White Sea, and known as the Murman coast. About a dozen *Vœrs* are scattered along this district: they are small, far apart, and miserable as harbours. The Russian fishery is not, therefore, of much consequence as a source of steam-prepared cod-liver-oil supply, except in those rare years when the *Lodde* fishery in Finmark happens to be a failure, which occurs only when the caplin do not visit the Norwegian coast, but for reasons unknown go farther east, to the Murman coast. In former times when this took place the Norwegian fishermen used to betake themselves to the Russian coast, but recently they have been forbidden to fish there, although the fishermen from that country had always been allowed to pursue their calling without let or hindrance in Norway. This rather selfish proceeding on the part of the Russian authorities has not, however, turned out to their advantage, for it has resulted in the practical destruction of their fishery as a source of medicinal cod-liver oil; and our factor, Mr. Östensvig, who visited and reported upon the region a few years ago, found only a few small steam factories in operation, and their produce was neither large nor good. The caplin never goes east of the *Vœr* known as Korabelnaja, and all the *Vœrs* farther east, that is, from Feretika to Litza, close to the White Sea, are utilised only for the summer fishery, when coal-fish and halibut are taken, but scarcely any cod-fish.

*Adulterations of Cod-liver Oil.*—As will be seen from the above, Norway has practically a monopoly of the steam-prepared cod-liver oil. No other country has the same advantages for carrying out the process properly, and if these advantages are fully utilised it is but natural that Norwegian oil should hold the field. Certainly the oil produced under such favourable conditions ought to be the very best, and on the whole it has attained a standard of which the Norwegian manufacturers have every reason to be proud. But, nevertheless, there is no doubt that latterly there has been a noticeable tendency to deterioration of quality even in Norwegian oils. The reason for this is not far to seek. The steam process requires conscientious working; anything that is gained in *quantity* is always lost in *quality*, and the low prices which have ruled of late years have been a strong inducement to squeeze more and more oil from the livers, and not to be over particular as to their quality, or even as to the kind of fish from which they are taken. At Lofoten and Romsdalen the use of livers other than those of the cod is out of the question, because no other fish are caught there; but in regard to the selection of livers of proper quality the less said the better. In Finmarken the matter is entirely different. The making of cod-liver oil goes on all the year round, but except during the unimportant spawning fishery the livers of codfish are by no means the only raw material available for the caldron. Great quantities of haddock, coal-fish, hake, torsk, ling, halibut, and wolf-fish are caught, and last, but not least, there is the porbeagle and the Greenland shark—a single liver of the latter being often equal in bulk to two barrels of cod's liver.

The Finmark manufacturers are thus subject to a temptation which does not exist at Lofoten or Romsdalen, and whilst, without doubt, there are honourable men amongst them, there are also others who are afflicted with a singular inability to distinguish between the livers of the cod-fish and those of other fish. Their ideas as to what constitutes cod liver are not unlike the rule laid down by the railway porter regarding dogs: 'Cats is dogs, and rabbits is dogs, and a parrot is a dog.' This confusion of ideas is, of course, most marked in years of scarcity, and when the writer has happened to be in Finmarken at such seasons he has himself seena nything that could possibly serve as an apology for a cod liver thrown into the caldron, shortly afterwards to emerge as *purest Norwegian cod-liver oil from carefully selected livers!* These remarks do not apply to the oil made in Finmarken during the *Lodde* fishery—at least in ordinary years. By far the greater number of the fish taken at this particular season are cod. There are frequently, also, considerable quantities of haddock, but of other fish there are very few until later in the year. The circumstances, therefore, do not allow of much adulteration before the end of the *Lodde* fishery. The only possibility of any importance is the addition of some haddock-liver oil, and it is not so objectionable as the other varieties. Indeed, in appearance and taste it can quite compare with cod-liver oil, but of course its therapeutical value is quite another question.

Bleaching in the sun is a process that is used for two distinct purposes. It is resorted to in order to improve the appearance of first-class oils. The oil is naturally a very pale yellow, on account of the presence of a pigment, lipochrome, concerning the chemical nature of which almost nothing is known. Like most organic pigments it is destroyed by the action of the sun's rays, and therefore good oils are sometimes bleached as if to make them look better than the best. If this is done very carefully at a low temperature, and never extended beyond a couple of hours, possibly no great harm may result. In the opinion of the writer, however, it should never be attempted, because the bleaching process not only destroys the lipochrome but also promotes decomposition of the oil itself, and the formation of products which are useless therapeutically, and may in addition irritate the stomach and disorder the digestive processes. An oil that has been bleached in this way can always be detected, at least by the experienced. It may, indeed, be perfectly colourless, but has a certain dull, faded appearance, due to the loss of the refractive power, which gives the unbleached oil a characteristic brilliancy.

The attempts to decolourise good oils are decidedly objectionable, but a much stronger term would be required for the second purpose for which bleaching is used—decolourising inferior steam-prepared oils in order that they should pass as first-rate products. The darker colour of such oils is not caused by the presence of lipochrome, but of decomposition products formed from the liver either before or during the process of preparation. The sunlight, which destroys the lipochrome, will at the same time form coloured decomposition products from the livers, probably from some of their albuminous constituents, and if they have been exposed to its rays for a couple of hours no really good oil can be produced from them. The same result follows when the livers are kept too long, or when the temperature is high, and also when during the melting process the livers are heated too long or too much. Now, most unfortunately, it happens that after the removal of the albuminous substances, these colouring matters can be destroyed by the further action of the sun's rays, and, provided the oil is not *too* dark, it may be bleached so as to resemble a colourless and therefore, as some people suppose, an irreproachable oil. As a matter of fact an oil doctored in this way is infinitely worse than the worst specimens of brown oils. These are honest productions, having no pretensions to be anything except what they really are, whilst, on the other hand, the oils artificially made colourless profess to be first class, and yet contain, not only their original, though decolourised, decomposition products, but, in addition, all those formed during the bleaching process.

The above account covers all the sins of the Norwegian makers of cod-liver oil. They may not always be so particular as they ought to be in selecting livers that are perfectly healthy; they may occasionally use livers that never grew inside a cod-fish; they may try to get more out of the livers than they should get; and they may attempt to improve the appearance of their oil by bleaching it; but the writer can say with confidence that this is all; and that no Norwegian manufacturer adulterates his oil with animal products other than those mentioned, or with vegetable or mineral oils. The writer ought, however, to make one proviso—that his statements apply only to Norwegian oils as they exist *in Norway*. When they leave the land of their production the makers, as a rule, cease to be responsible for them. Most of the oil is sent to Hammerfest or Bergen, and thence exported to Hamburg, London, or New York, where it is sold and lost sight of until it again appears, often in a beautified form, and labelled 'virgin drippings,' 'first grades,' 'from carefully selected livers,' 'prepared by an entirely new process,' &c.

## PETER MÖLLER'S NEW PROCESS

Cod-liver oil is undoubtedly one of the most valuable medicinal agents known to man. Its value has one remarkable proof in the fact that it was extensively used in the days when only the brown variety could be obtained. In those days cod-liver oil was not a desirable article of consumption; indeed, to put the matter plainly, it was an abomination, and no one could have taken it willingly, even once, not to speak of day after day and month after month. Nevertheless many people did take it, and the only reasonable explanation is that the oil must have given strikingly favourable results; otherwise, medical men would not have been justified in prescribing it, nor could their patients have been induced to use it.

But although cod-liver oil was thus highly esteemed, despite its very objectionable characters, these, there is no doubt, were a great drawback to its successful administration. The class of patients to whom the oil is given, or at all events to whom it is useful, are cases with, broadly speaking, defective nutrition, and, therefore, exactly the cases which can least afford to risk any disturbance of the digestive apparatus. Yet this was the very thing that the old, badly prepared cod-liver oil was most apt to do. It was not only disagreeable to the palate, but it was also intensely irritating to the stomach, and often it must have been a question whether its administration did not do more harm than good.

These highly objectionable characters of the old cod-liver oil were due to the fact that it was not the oil pure and simple, but the oil with something added to it. This something was the cause of the greater part of the trouble, and, not to mince the matter too finely, it was nothing more or less than an extract of rotten livers. The oil was obtained in those days simply by allowing the livers to putrefy, when the decomposition of the albumens resulted in the breaking up of the cells, and the escape of the oil globules contained in them. It also, however, resulted in the formation and inclusion in the oil of a large variety of putrefactive products, part of which has recently been found to consist of poisonous ptomaïnes. These, even up to the present day, are called, 'active principles' by some people, but we need hardly add that an admixture of poisonous ptomaïnes, both quantitatively and qualitatively uncontrollable, is not a desirable addition to any medicinal remedy, and perhaps least of all to cod-liver oil, seeing that it is much more a food substance than a medicine. If they are present in the oil they render it not only disgusting to the patient, but they also make it quite as likely to hurt as to help him.

A generation or two ago the brown oils were the only kind that were made or that could be obtained, and the people of the present day who have to take cod-liver oil may be thankful that, in regard to this at least, they live in happier times. All the disagreeable and detrimental qualities of the oil due to decomposed albumens were removed by the introduction of Möller's early process. The livers were no longer left to rot till the oil exuded, but the oil was drawn off from them while they were yet perfectly fresh. Putrefactive products were, of course, an impossibility in oil made in this way—provided the process was properly carried out.

The real cod-liver oil—that is, the oil without the extract of rotten livers—was clear in colour, practically free from the nauseating taste and smell, and consequently, in comparison with the old oil, it was a thing of delight from the consumer's point of view. From the doctor's point of view it was also an improvement of no small importance. Not only could it be given without upsetting the patient, but in addition *it was cod-liver oil pure and simple*: its therapeutical effect could now, and for the first time, be obtained in its greatest perfection and to its fullest extent, and this without any drawback whatsoever—except one.

Peter Möller introduced his invention in 1853, calling it, with characteristic modesty, not by his own name, but simply 'the steam process of preparing cod-liver oil.' The colourless oil produced by it was so completely different from the brown oils then in use, that there was no small difficulty, at first, in getting people to believe that it was cod-liver oil at all. But as soon as they became convinced that it was really so, the advantages it possessed were so great and so obvious that in a few years it was practically the only oil in use.

The product of the steam process was thus a vast improvement upon the older oils with their putrefactive ptomaïnes and their sickening taste and smell, but it was not perfect. The advance made by Peter Möller's invention was so great that no other improvement in the manufacture of cod-liver oil can possibly equal it; yet the oil produced by it is capable of a considerable alteration for the better. The new cod-liver oil had indeed lost the objectionable taste and smell of the old oil, but it still retained one objectionable character, and that one perhaps the worst of all—the property of causing nauseous eructation. This most disagreeable symptom has seemed to be more or less inseparable from even the very best steam-prepared oils, and Heyerdahl's investigations have shown that it is dependent upon certain chemical bodies which cannot from their nature by any possibility be *eliminated* from the oil though prepared by means of Möller's *original* process.

The disagreeable taste and smell of the older oils were, as we have said, due to decomposition products derived from the putrefaction of the livers; but the constituents causing eructation are derived from quite a different source. They are not broken-down albumens, but oxidised fats—products derived, in fact, from the oil itself. Some oils contain such products in a fully developed form: these are rancid oils. Other oils contain them in a more or less potential form, and these may be almost tasteless, till they reach the stomach, when they immediately become quite otherwise. Now, an oil distasteful to the palate is certainly bad enough, but not nearly so bad as an oil which, although, perhaps, tasteless when taken, may become unspeakably abominable when it reaches the stomach. Why it becomes so is easily explained: such oils do not remain passive in the stomach, but the irritation they produce sets up eructation and brings the taste up to the mouth, where it asserts its unwelcome flavours, not once only, but again and again, till the unhappy patient may be completely upset and firmly convinced that if it is to be at the expense of taking cod-liver oil, life is not worth living.

Such a conclusion as this is not unfrequently come to by patients who might be greatly benefited by cod-liver oil, while others—those who force themselves to take the oil—do so only by a great and, from a medical point of view, very undesirable effort. Thus, for both classes, this remaining drawback is a serious one, and its removal is a matter of no little importance to them, and to all who are interested in cod-liver oil. Many attempts have been made to remove it, but up to the present without success. In fact success was not possible where the efforts were misdirected: these attempts, so far at least as they have come under our observation, have been made under an entire misapprehension of what had to be done, and therefore in an entirely wrong direction. We cannot here enter into all the details of these well-intentioned efforts, as they are discussed in another section of this work, but, generally speaking, they aimed at the production of an agreeably tasteless or pleasantly flavoured *preparation* of cod-liver oil. The eructation-producing property of the oil need not, however, have any connection with its taste, unless present in a high degree, and consequently these preparations were not likely to be successful. As a matter of experience they have not been so, and their highest achievements have been to make the oil agreeable, or at least not disagreeable, *to the palate.* This may be a laudable result in itself, but it is to be noted that it is so only in regard to inferior oils, for an oil properly prepared by Möller's method should have no unpleasant taste, even to the most fastidious.

We have not been unmindful of the importance of the question, and have not been altogether idle; indeed, we feel under an obligation to do everything in our power to solve it. The late Peter Möller devoted the best part of his life to the task of improving the methods of preparing cod-liver oil. The processes he invented and introduced constituted the only real advances which have been made in the matter and were an immense improvement in the oil; from being the crudest product it became, *with the exception of this single drawback*, the most perfect product imaginable. The efforts made by Peter Möller did not succeed in removing the drawback, and the least that we, his successors, could do was to take up his nearly, but not quite, finished task and endeavour to bring it to its legitimate and successful conclusion.

Practical experience had convinced us that the taste of cod-liver oil had not necessarily anything to do with its property of disordering the stomach and causing eructation. The evil taste and smell of the oil prepared after the old methods were due to the putrefactive products thereby added to it, and when these were absent the oil might have been absolutely without taste or smell—but still capable of causing eructation. It was thus evident that all the efforts made to overcome this difficulty by covering the taste of the oil were quite beside the mark. Of course, the taste of the oil when taken in no way influences the taste of the eructations, and no matter how pleasant the former may be made, the latter will be quite different.

Our early efforts were directed to bringing the steam process to its fullest perfection, and, although they did not fully lead to the desired object —an oil which would not cause eructation —they certainly did teach us two things; first, that *it is of no use whatever to try to improve the oil once it is made, and consequently that the improvement must be in the manufacturing process*; and secondly, *that the oil which has been exposed to the lowest possible heat for the shortest possible time possesses in a lesser degree the objectionable quality.* But to produce an oil entirely free from the tendency to cause eructation seemed quite impossible, and it was asserted that this property was essential to the oil—part and parcel of it, in fact.

We did not forget that before the introduction of the steam process exactly the same statement had been made regarding the brown colour and objectionable taste and smell of the oil, and therefore the prevailing opinion was not permitted to influence in any way the efforts we were continuing to make to overcome this remaining difficulty.

To minimise the objectionable quality we, in the meantime, laid down the rule that *the livers were not to be subjected to a temperature exceeding* 70° *C., and even that for only* 45 *minutes.* Of course this proved a costly method, because the quantity of oil that exudes during that time and at that low temperature is comparatively small, and the result was that many manufacturers found themselves unable to keep to this standard. Indeed the low prices to which cod-liver oil has been brought by absurd competition, and unjustifiable methods of production, have made such a standard impossible for makers who find that cheapness is a necessary element required to obtain a market for their oil.

Apart from its costliness, however, the process, even in its highest perfection, was not *entirely* successful, and in the year 1880 we became convinced that everything had been done in *this* direction that could be done, and that *our object could only be attained by striking out in an entirely new direction.* This was accordingly done, and with results which we now wish to bring before all who are interested in a matter of such importance.

Until about fifteen years ago the chemistry of fats was practically an unexplored field, and none of our present more exact methods of examining and analysing these bodies was then available. This was the first difficulty that confronted us when we came to the conclusion that having exhausted *the art*, we must fall back on *the science*, of preparing cod-liver oil. We did not, however, allow that to deter us from carrying out the plan upon which we had determined, and we are able to state now that, in regard to cod-liver oil at least, the difficulty of scientific analysis is greatly minimised. The knowledge of the chemistry of fatty bodies has immensely increased since 1880. Many investigators have devoted themselves to this particular department of chemical science, and the results which they have obtained are not only of great scientific interest, but many of them are of equally great practical importance.

In the year 1857 Peter Möller, in a paper[1] read before the congress of Scandinavian scientists at Christiania, expressed his opinion that the fatty acids of cod-liver oil differ essentially from the fats derived from other sources. As time went on this opinion was, more and more, confirmed by the marked differences which our investigations revealed between cod-liver oil and oils containing the ordinary fatty glycerides, the characters of which were, however, pretty well overlooked by analytical chemists. Möller's opinion was only an opinion, and at that time incapable of scientific demonstration; but the progress of organic chemistry has shown that he was, nevertheless, perfectly correct.

The investigations commenced by us in 1880 have been directed chiefly to clearing up the problems connected with the chemistry of cod-liver oil and the other oils allied to it, and this work has been conducted by Mr. P. M. Heyerdahl. To his enthusiastic and unwearied efforts not only we, but all who are interested in the subject owe a deep obligation. The results attained by him stand *facile princeps* amongst the many notable additions made during the last few years to our knowledge of the chemistry of fats, and, so far as they bear upon the nature of cod-liver oil, they are simply the *scientific* corroboration of Peter Möller's expressed opinions. What they have shown and proved is briefly this: *the acids which form ordinary fats—that is, the acids of oleïn and stearin—do not exist in cod-liver oil, but there are instead, at least, two glycerides, which so far have not been found anywhere else.*

Apart from its scientific interest, the practical importance of this discovery is so obvious that we need not insist upon it. It throws the first real light on the nature of cod-liver oil, and enables us to comprehend how that oil possesses *a peculiar physiological action not possessed by other oils*, and thereby exercises a therapeutical influence which is *sui generis.*

These new fatty acids have been named *therapic acid* and *jecoleïc acid.* Their properties, from the chemical point of view, have been as far as possible investigated and determined, and the results show that, compared with the ordinary fatty acids, these bodies possess several remarkable and very suggestive characters.

Therapic acid is a compound *with four double bonds*, and consequently it belongs to the tetra-ethylene series, of which it is the first and only representative as yet discovered, not only amongst the fatty substances, but, indeed, amongst any chemical compounds. This is certainly a most remarkable fact, and at once suggests the possibility of *essential differences, physiological as well as chemical, between therapic acid and the other fatty acids.* It is also an interesting circumstance that therapic acid is the only member of the margaric acid group which has yet been found as a product of living animal nature. In addition to its chemical constitution, therapic acid is distinguished by the astonishing facility with which it attracts, and is split up by, oxygen, iodine, bromine, and other agents, even at ordinary, and still more at higher, temperatures.

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[1] *Om Tilvirkningen of Torskelevertran i Almindelighed og om en ny Maade for Tilvirkningen of Medicintran, Christiania,* 1857.

In his investigations Mr. Heyerdahl found it absolutely necessary to protect the acid from the inroads of oxygen, which was done by conducting all the analytical processes under a current of hydrogen. The instability of the acid defeated all attempts at isolating it in the uncombined form, but the bromine combination product in which the unsaturated compound is transformed into the saturated octa-bromo-margaric acid was found to be sufficiently stable for closer examination, and through it the chemical constitution of the acid was investigated and determined.

Apart from the scientific interest of this discovery, it was of immense practical importance to have determined the presence in cod-liver oil of a fatty acid so very unstable in its nature. This indeed gave us the key to the problem we had been endeavouring to solve, *pointing out to us both the cause of the eructation producing property of cod-liver oil, and the general direction of the steps necessary to remedy it.*

Methods devised to give an exact quantitative analysis of the hydroxylated therapic acid present in cod-liver oil made it possible to estimate the bearing of these hydroxy-acids on the production of eructation, and it was found that *the hydroxy-acids were the cause of eructation, and that this unpleasant symptom was more or less marked according to the quantity in which they were present.* Cod-liver oil containing no hydroxy-acids caused no unpleasant eructation whatever.

The rapid oxidation of the fatty acids of cod-liver oil was strikingly brought out by a difficulty that arose during Heyerdahl's first attempts to estimate the amount of hydroxy-acids in the oil. No constant results could be obtained, and even samples taken from the same parcel of oil gave results that were sometimes utterly divergent. When a careful comparison was made of the long series of estimates, he found that, other things being equal, the more time an analysis occupied, the more hydroxyls there were. This could be ascribed only to a very rapid oxidation of the fatty acids when exposed to the air during the analysis, and the lesson taught thereby, in regard to preparing the oil was obvious.

When the process of estimation had been perfected, so that absolutely reliable results could be obtained, it was ascertained that even the very best steam-prepared oils contained hydroxyls, their acetyl value being about 2; which corresponds to 0·15 per cent. of hydroxy-acids. This was the minimum obtainable by the most careful application of the steam process and the slightest increase of time during which the livers were exposed, or the use of even slightly higher temperatures, caused a marked increase in the acetyl value of the oil produced.

Cod-liver oil with an acetyl value of only 2 may cause marked eructation, and it was evident that, even at its very best, the steam process was in this respect a partial failure: it could not give an oil *sans peur et sans reproche.* But Heyerdahl's researches had now clearly shown us that this was not an inherent property of the oil, as formerly believed, and that an oil entirely free from this mischievous quality might be produced. If during the process of manufacture the fatty acids of the oil were never allowed to come in contact with oxygen, the oil would be absolutely free from the objectionable hydroxy-acids, that is, free from the one practical difficulty that yet stood in the way of administering cod-liver oil.

The oil carefully prepared for experimental purposes under a current of hydrogen did not contain a trace of hydroxyls. It was, in fact, cod-liver oil pure and simple, and the first that had ever been seen; for, everything produced before had contained, not only the pure fats of the oil, but also in greater or lesser degree their oxidation or decomposition products—the hydroxy-acids. *From the chemical point of view we had now reached our ideal oil, and a series of careful experiments satisfied us that from the physiological point of view it was also the ideal—an oil incapable of causing irritation of the stomach and, consequent, eructation.* This result, answering our most sanguine expectations, and justifying the years of work that had led up to it, was certainly most gratifying to all who had looked and laboured for it, but it left us with another problem to solve before we could practically realise our object. To produce this perfect oil in very small quantities for scientific purposes was now, comparatively easy; to produce it on a commercial scale was altogether a different matter. This last and only remaining obstacle necessitated many experiments, naturally accompanied by many failures, but at length the difficulties were overcome, and *we were successful in devising an apparatus by which we could produce cod-liver oil on a large scale without allowing even the slightest oxidation to take place.* The apparatus eventually adopted is so designed that the air can be completely excluded from it during the whole operation from beginning to end, the process being conducted in a current of carbonic acid from the moment the livers enter the apparatus until the oil obtained from them is safe within the bottles.[1]

We have subjected the oil obtained by this process to a series of most carefully carried-out investigations, with results so excellent and so uniform that we are perfectly satisfied that at length our object has been attained. For years our investigations, whatever their value from the scientific side, were, from the practical aspect, of little value when compared with the results of to-day.

The product, *the Hydroxyl-free Cod-liver Oil*, seems to all intents and purposes perfect—without either the peculiar smell or oily taste, and without that most obnoxious of all the real or imaginary characteristics of cod-liver oil, the property of causing loathsome eructation; and we do not think that we go too far in saying that IT IS THE FIRST AND ONLY REAL IMPROVEMENT IN THE METHOD OF MANUFACTURING COD-LIVER OIL SINCE 1853, WHEN PETER MÖLLER INTRODUCED HIS STEAM PROCESS.

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[1] The method has been protected by letters patent in the different countries.

# PHARMACEUTICAL ANNOTATIONS

A volume of no small extent might be written on the pharmacy of cod-liver oil, for that unfortunate article has been 'prepared' by methods which are only as numerous as, in the opinion of the author, they are uncalled for. Many of these methods are now matters of history, but, of course, each was supposed to be an improvement on the oil itself, although in some cases going so far as to improve it out of existence. A full account of all the past and present ways of pharmaceutically preparing cod-liver oil is here out of the question, and all that the writer will attempt shall be a brief description of some instances of the more interesting or more important methods that have been used.

## Flavourings

Before the introduction of 'elegant preparations' of cod-liver oil, that is, in the period when the light-brown varieties had full sway, it was found desirable, if not indeed necessary, to cover the taste of the oil by adding various flavouring agents. After the steam-prepared oil had practically displaced the darker kinds the practice was continued, and still is, although as a matter of fact it should be quite unnecessary—*if the oil be pure and properly prepared.*

Some of these flavouring agents or *corrigentia* are very curious and interesting, and we may here give a brief selection of them.

As far back as 1775 it was found difficult to make the patients in Manchester Infirmary swallow the light-brown oil; and we are told that the vehicle in which they most preferred to take it was warm beer (*British and Colonial D.* vol. xxii. p. 453, from *Med. Press*—Hutchinson's *Archives*).

We next find that iron-water, prepared by macerating rusty nails, is recommended to be taken immediately after the oil, the taste of the oil and of the eructations being thereby agreeably changed into 'the flavour of oysters' (*Rec. de méd. et chir. milit.*).

Chevrier, Paris: Ol. morrh. balsam.—Pix liquid 1 part, bals. tolut. 3 parts, syr. sacchari 4 parts, sp. v. rect. 4 parts. Digest for four hours and then shake with ol. morrh. 1,000 parts. Separate the clear oil.

Hager recommends an addition of oil of peppermint 1 part, and 5 parts of chloroform to 600 of cod-liver oil (*Pharmaceutische Centralhalle*, x. 15).

Pavesi—40 parts of cod-liver oil digested with two of roasted coffee and one of animal charcoal (*Giorn. di farm.* 1870).

Duguesnel.—Flavouring with 1 per cent. of eucalyptus oil (*Bull. gén. de thérap.* 1883).

Another recipe is: Wood-tar 4 parts, sol. of ammonia 20 parts, oil 1,000 parts. First shaken and then boiled as long as ammonia is given off; after cooling, 8 drops oil of anise are added (*Ph. C.* xxv. 546).

A. Ferguson, jun.—The oil to be combined with the fruit of cacao, or with the usual ingredients of cocoa or chocolate. This idea was thought so valuable as to be worth a patent—No. 4495, 1880.

R. F. Ferguson.—One part of tomato or walnut ketchup to be added to 4 parts of oil.

The same authority also recommends the following mixture: Liebig's extract 8 parts, extract of celery seeds 1 part, vinegar 16, water 32, and cod-liver oil 80 parts (*Amer. Journ. of Pharm.*, through *The Chemist and Druggist*, xxxiii. p. 167).

Dr. Fonssagrives.—Cod-liver oil 96 grm., iodoform 20 centigr., and essence of anise 4 drops. 'The taste and smell of the oil are completely masked,' but, 'should it still be repugnant,' we are recommended to take it with 'a small dosis' (? a grain) 'of salt' (*Gaz. des hôpit.* 1882).

Lastly we may mention the combination of cod-liver oil with saccharine: Saccharine 40 centigr., acetic ether 2 grm., cod-liver oil 100 grm., peppermint or cinnamon oil q.s. Dissolve the saccharine in the ether and add cod-liver oil, little by little, with frequent agitations; finally add peppermint or cinnamon oil (*Wiener klinische Rundschau*).

## Liniments, Jellies, and Emulsions

The next development in the art of masking and disguising cod-liver oil was by incorporating it into liniments, jellies, and emulsions. So far as the writer is aware, the liniments were originally German inventions, jellies French, and emulsions American.

*Liniments.*—These are made very much in the same way as linimentum calcis.

The first that we have found is oleum morrhuæ calcinatum, a Viennese preparation dating from 1868, and consisting of equal parts of oil and lime-water.

Even as late as 1889 we find Lefaki recommending this liniment with the addition of some palatable syrup. He confidently asserts that the oil in this form does not stick to the palate and leaves no after-taste (*Therap. Gazette*, 1889, p. 488).

*Jellies.*—A jelly, *crème d'huile de foie de morue*, appeared some twenty-five years ago in Paris. It was prepared from cod-liver oil 460 parts, sugar 150 parts, white of eggs 200 parts, heated to 40°, mixed with 100 parts of a solution (1-40) of gelose (Chinese gelatin, parabin) and 50 parts of aqua amygd. amar (Leroy, *Ph. C.* ix. 319).

Up to the present there seems to be a craving for jellies; for as late as 1890 we find a formula:—

| | |
|---|---|
| Gelatin | 2 oz. |
| Water | 15 „ |

Soak over night. Add

| | |
|---|---|
| Syrup | 10 oz. |

Melt over a water-bath, then pour into a mortar containing

| | |
|---|---|
| Cod-liver oil | 25 oz. |
| Chloroform | 20 ♏ |
| Oil of cinnamon | 5 „ |
| „ bitter almonds | 3 „ |

Stir until the fluids assume a uniform appearance, then pour into bottles, before cooling (*Ch. & D.* xxxvi. p. 26).

*Emulsions.*—Nearly everything capable of emulsifying cod-liver oil has been called into requisition, such as gums, eggs, dextrin, malt, moss, quillaia, etc.

The following are specimens of the different sorts:—

### Simple Emulsion with Gum Acacia

| | |
|---|---|
| Cod-liver oil | 4 oz. |
| Powdered gum acacia | 1 „ |
| Saccharine (made into a 10-per-cent. solution by adding 8 grains of sodium bicarbonate to 20 grains of saccharine and water q.s.) | 2 gr. |
| Oil of cassia | 4 ♏ |
| „ bitter almonds | 4 „ |
| Water to make | 8 oz. |

Mix the oils with the gum in a dry mortar, add the saccharine solution and 2 oz. of water, stir till the emulsion is formed, and finally add water to make 8 oz. (Gerrard's formula, *Ch. & D.* xxxi. p. 646).

---

### Emulsion with Gum Acacia and Hypophosphites

These are chiefly represented by 'proprietary articles.' The following are different analyses of the same compound:—

| | |
|---|---|
| Cod-liver oil | 35·5 parts |
| Glycerin | 18·5 „ |
| Hypophosphite of calcium | 1·0 „ |
| „ „ sodium | 1·0 „ |
| Water | 42·0 „ |
| Gum acacia and flavouring | q.s. |

(Accord. to 'New Idea.')

| | |
|---|---|
| Cod-liver oil | 24–25 parts |
| Glycerin | 20–21 ,, |
| Hypophosphites of calcium and sodium | 2 ,, |
| Water | 44 ,, |
| Gum acacia | 11–12 ,, |

(Average of four analyses by Dr. Hermann Hager.)

### Emulsion with Gum Acacia, Hypophosphites, Iron, and Manganese

| | |
|---|---|
| Cod-liver oil | 16 oz. |
| Sugar | 4 ,, |
| Gum acacia | 2 ,, |
| Hypophosphite of calcium | 200 gr. |
| ,, ,, sodium | 120 ,, |
| Ferrous sulphate | 76 ,, |
| Manganous sulphate | 38 ,, |
| Oil of bitter almonds | 6 ♏ |
| ,, cloves | 2 ,, |
| Essence of vanilla | 5 ,, |
| Water | q.s. |

Dissolve the sulphates in 2 oz. of hot water and 15 drops of hypophosphorous acid; add 80 grains of hypophosphite of calcium; stir well and bring to the boil, then filter and wash the filter and contents with hot water to 3 oz.; in the filtrate dissolve the remainder of the hypophosphites. Place the gum and sugar in a mortar, mix the oil with them thoroughly, and add 8 oz. of water, triturating thoroughly. Then gradually add the hypophosphite solution, the flavour, and sufficient water to make 30 fl. oz. (*Ch. & D.* xxix. p. 563.)

*Cod-lactone* is an emulsion to which is added lacto-phosphate of lime (*Ch. & D.* xliii. p. 598).

### Emulsion with Tragacanth and Hypophosphites

| | | |
|---|---|---|
| Cod-liver oil | | 40 oz. |
| Powdered tragacanth | | 200 gr. |
| Tincture of benzoin (1–10 rectd. spirit) | | ½ oz. |
| Spirit of chloroform | | ½ ,, |
| Glycerin | | 2 ,, |
| Oil of bitter almonds | | 40 ♏ |
| ,, lemon | | 40 ,, |
| Distilled water | | 80 oz. |
| Calcium hypophosphite | 10 drms. | 40 gr. |
| Sodium ,, | 2 ,, | 40 ,, |
| Potassium ,, | | 80 ,, |

Place the oil in a Winchester quart and pour into it the powdered tragacanth, tincture of benzoin, and spirit of chloroform mixed; agitate briskly for one minute, then add, all at once, a pint of distilled water and agitate as before; lastly add the oils, glycerin, and remaining water in which the hypophosphites may be dissolved, or added to the emulsion afterwards as required (Baily's formula in 'Physicians' Pharmacopœia,' *Ch. & D.* xxx. pp. 305, 341).

### Emulsions with Gum Acacia and Tragacanth

| | |
|---|---|
| Powder of tragacanth | 15 gr. |
| ,, ,, gum acacia | 15 ,, |
| Syrup | ¼ oz. |

rubbed into a paste, add

| | |
|---|---|
| Water | 1½ oz. |

Rub into a good mucilage, and add by a thin stream

| | |
|---|---|
| Cod-liver oil | 2½ oz. |
| Essence of lemon | 12 ♏ |
| Essent. oil of almonds | 2 ,, |

These being well incorporated, add gradually

| | |
|---|---|
| Distilled water | 2½ oz. |

And lastly add cautiously

| | |
|---|---|
| Rectified spirit | ¾ oz. |

The excellency of the emulsion is in proportion to the diligence of the operator in using his pestle and mortar (*Squire's Companion*, 1894).

| | |
|---|---|
| Powdered tragacanth | 800 gr. |
| ,, gum acacia | 1,200 ,, |
| ,, arrowroot | 800 ,, |

Rub well in a mortar with

| | |
|---|---|
| Cod-liver oil | 80 fl. oz. |

till consistency of cream; transfer to a 3-gallon bottle and add, all at once, a mixture of

| | |
|---|---|
| Glycerin | 10 oz. |
| Water | 70 ,, |

Shake well for 10 minutes and then pour in

| | |
|---|---|
| Spirit of chloroform | 2½ oz. |
| Oil of lemon | 160 ♏ |

Shake again well (*Ch. & D.* xxxiii. p. 388).

### Combination of Liniment and Tragacanth Emulsion

| | |
|---|---|
| Powdered tragacanth | 2 drms. |

Rub up with

| | |
|---|---|
| Glycerin | 2 oz. |

and add

| | |
|---|---|
| Boiling water | 8–10 oz. |

Make into a firm jelly, and when cold add gradually

| | |
|---|---|
| Cod-liver oil | 40 oz. |

previously mixed with

| | |
|---|---|
| Lime-water | 15 oz. |

Finally add

Oil of almonds . . . . . 20 drops

dissolved in

Rectified spirit . . . . . 2 oz.

An addition of 2 grains of chloride of sodium to each ounce of emulsion will improve the emulsion and make it more palatable (*Ch. & D. Diary*, 1881).

### EMULSION WITH PANCREATIN

Many preparations have been made with the avowed object of increasing the efficiency of cod-liver oil by the addition of pancreatin. One of the first of these, an American preparation, was dignified by the name Hydroleïne. So far as the writer knows, this is now extinct —at least on this side of the Atlantic. It was, according to the label accompanying it—

| | |
|---|---|
| Soda | 0·3 part |
| Boric acid | 0·2 ,, |
| Water | 30·0 ,, |
| Pancreatin | 4·0 ,, |
| Hyocholic acid | 0·5 ,, |
| Cod-liver oil | 65·0 ,, |

The so-called hyocholic acid is probably nothing more nor less than bile. The name is a purely fancy one of American invention, and quite unknown to scientific chemistry; but the substance, whatever its composition may be, makes itself painfully *en évidence* to the olfactory and gustatory nerves when the preparation containing it has become sufficiently matured.

Hydrated cod-liver oil is an English edition of a similar composition. It also was known as hydroleïne, a proprietary medicine. 'The delicacy of adjustment' of its essential points, 'both in the chemical reactions and in the manipulation necessary to produce the required combination,' etc., 'is so great as to render it difficult of manufacture, even under the direction of so able a chemist as,' etc.—so says a booklet written in praise of hydrated oil by a gentleman with 'M.D.' after his name.

The brilliancy of this idea seems to be fascinating, for we find it revived in Germany in 1887. It is improved, of course, by the scientific acquirements of intervening years, and therefore taurocholates are substituted for bile, and olive oil for cod-liver oil, for which reason it will appear further on, under the heading of 'substitutes' and the name of *Pinguin*.

### EMULSION WITH EGGS

| | |
|---|---|
| Yolks of eggs | 2 |
| Powdered sugar | 4 oz. |
| Oil of bitter almonds | 2 drops |
| Orange-flower water | 2 oz. |

Mix and add an equal bulk of cod-liver oil (*Ch. & D.* xxx. p. 83).

### EMULSION WITH EGGS, RUM, AND PHOSPHORIC ACID (A WASHINGTON FORMULA)

| | |
|---|---|
| Dilute phosphoric acid (U.S.) | 1½ oz. |
| Yolks of eggs | 3 |
| Cod-liver oil | 8 oz. |
| Glycerin | 2½ ,, |
| Oil of bitter almonds | 20 ♏ |
| New England rum | 8 oz. |
| Orange-flower water to make | 2 pints |

(*Ch. & D.* xxxii. p. 281.)

Apparently the tragacanth emulsions, in spite of the praise lavished upon them on their first appearance, have proved no more satisfactory than the egg emulsions, because we find some years later attempts being made to improve upon them *by combining the two.*

### EMULSION WITH TRAGACANTH AND EGGS

| | |
|---|---|
| Powdered tragacanth | 24 gr. |
| Yolks of eggs | 2 |
| Hypophosphite of calcium | 48 gr. |
| ,, ,, sodium | 48 ,, |
| Glycerin | 1 oz. |

Rub together in a mortar. Add in their order, and in the proper manner for making an emulsion

| | |
|---|---|
| Orange-flower water | 2 oz. |
| Cod-liver oil | 24 ,, |
| Oil of bitter almonds | 15 ♏ |
| ,, cinnamon | 25 ,, |
| Chloroform | 10 drops |
| Saccharine | 5 gr. |

dissolved in

| | |
|---|---|
| Jamaica rum | 5 drms. |
| Make up with orange-flower water to | 36 fl. oz. |

(*Ch. & D. Diary*, 1890.)

Another formula in which there is 50 per cent. of cod-liver oil, as against 66·6 per cent. in the preceding one:—

| | |
|---|---|
| Cod-liver oil | 8 oz. |
| Yolks of eggs | 2 |
| Powdered tragacanth | 16 gr. |
| Elixir of saccharine | 1 fl. drm. |
| Simple tincture of benzoin | 1 „ |
| Spirit of chloroform | 4 „ |
| Essential oil of bitter almonds | 8 ♏ |
| Distilled water to make | 16 oz. |

Measure 5 fl. oz. of water, place the tragacanth in a dry mortar, and triturate with a little of the cod-liver oil; then add the yolk of eggs and stir briskly, adding water as the mixture thickens. When of a suitable consistency add the remainder of the oil and water alternately with constant stirring, avoiding frothing. Transfer to a pint bottle, add the elixir of saccharine tincture of benzoin, spirit of chloroform, and oil of almonds, previously mixed; shake well and add distilled water, if necessary, to make 16 fl. oz. (unofficial formulary, *British Pharm. Conference*).

## Emulsions with Malt Extract

The mixture of malt extract and oil is probably, also, an American idea. We give below the original formula and a couple of the so-called improvements upon it.

Equal parts are mixed by adding the oil to the warm extract in small portions, at first of 5 per cent., later 10 per cent. The mixture becomes at last so thick that water has to be added.

### Emulsions with Malt Extract and Pancreatin

| | |
|---|---|
| Cod-liver oil | 14·60 parts |
| Powdered gum acacia | 8·00 „ |
| Glycerin | 5·00 „ |
| Peptic substances | 0·10 „ |
| Pancreatin | 3–4·00 „ |
| Malt extract | 37·50 „ |
| Syrup | 18·50 „ |
| Water | 12–12·50 „ |
| Salicylic acid | 0·14 „ |

(Average of four analyses by Dr. H. Hager.)

This is one of the so-called solutions of cod-liver oil, their description as 'solutions' being an ingenious invention of our American cousins. The slightest acquaintance with the properties of its several constituents will suffice to convince anyone that there can be no possibility of a solution. It is no doubt useful for trade purposes to describe it thus, relying for proof upon an optical illusion. Under the microscope the appearance of the preparation is uniform, no oil globules being visible; but this is caused by the fact that the extract and the oil have nearly the same index of refraction. Just as, for the same reason, many bacteria long escaped detection by the microscope, but became visible when coloured, so the oil globules in the so-called solution become visible when coloured with wolframic or osmic acid, or simply by the employment of a small diaphragm. It will then be seen that the 'solution' is, in reality, an emulsion, and with oil globules which are certainly not smaller than those of any ordinary emulsions. The presence of salicylic acid is probably necessary for the preservation of the malt extract, but it must be therapeutically objectionable in many cases. Judging from Dr. Hager's analyses, the malt extract employed in the particular brand he examined is mixed with syrup.

The emulsion contains *cod-liver oil to the extent of only* 15 *per cent.*, according to the analysis.

Another of the improvements derived from malt extract and pancreatin with hypophosphites is—

### Pancreatic Emulsion

| | |
|---|---|
| Cod-liver oil | 8 fl. oz. |
| Extract of malt | 8 „ |
| Pancreatin | 256 gr. |
| Oil of gaultheria | 32 ♏ |
| „ cinnamon | 16 „ |
| Alcohol | 4 fl. drms. |
| Syrup of hypophosphites (U.S.), to make | 32 fl. oz. |

Beat the extract of malt in a mortar until it can be drawn into strings, add the pancreatin, and mix thoroughly. Then add the oil, in small quantities at a time, and beat until a smooth mass results. Add the alcohol and essential oils, then gradually incorporate the syrup by trituration. Here there is 25 per cent. of oil (*Amer. Drug.* 1886, No. 11).

Emulsions having once become the order of the day, everything that could make them has been introduced, and has had more or less of a run, as is the way with novelties. The following are some modern specimens:—

### Emulsion with Dextrin

| | |
|---|---|
| Cod-liver oil | 8 fl. oz. |
| Mucilage of dextrin (1 in 3) | 5 ,, |
| Syrup of Tolu | 2 ,, |
| Flavouring | q.s. |
| Water to | 16 fl. oz |

Add oil in small portions to the mucilage in a bottle, agitating each time; then flavouring, syrup of Tolu, and lastly water (*Ch. & D.* xxxiii. p. 768).

### Emulsion with Carrageen

| | |
|---|---|
| Decoction of carrageen moss | 100 parts |
| Cod-liver oil | 120 ,, |
| Sugar | 20 ,, |
| Aromatic oils | ad lib. |

made into an emulsion by beating, not by triturating (*L'Union pharm.* 1881, x.).

| | |
|---|---|
| Carrageen moss | 1 drm. |
| Make a decoction in a water-bath to | 5 fl. oz. |

and add

| | |
|---|---|
| Glycerin | 2 fl. oz. |
| Alcohol | 1 ,, |
| Oil of bitter almonds | 5 drops |
| ,, gaultheria | 3 ,, |

when cold add

| | |
|---|---|
| Cod-liver oil | 8 fl. oz. |

in three portions, shaking vigorously after each addition (*Pharm. Record; Ch. & D.* xxx. p. 581).

### Emulsion with Quillaia

| | |
|---|---|
| Cod-liver oil | 8 fl. oz. |
| Tincture of quillaia | 1 ,, |
| Syrup of Tolu | 2 ,, |
| Flavouring | q.s. |
| Water to | 16 oz. |

Put the tincture in a suitable bottle, add the oil, two ounces at a time, shaking thoroughly to ensure complete emulsification; then add the rest and shake again thoroughly (*National Formulary; Ch. & D.* xxxiii. p. 768).

### Emulsion with Condensed Milk

| | |
|---|---|
| Cod-liver oil | 8 parts |
| Condensed milk | 3 ,, |
| Glycerin or syrup | 3 ,, |
| Water | 2 ,, |

Milk rubbed in a mortar, oil added gradually; lastly glycerin and water (*Br. & Col. D.* xix. p. 162).

## Preparations with Cod-liver Oil

We have so far described the methods used to cover or disguise the disagreeable flavour of the oil, and in some cases the simultaneous incorporation of other compounds supposed to increase the therapeutical effect of the oil. We may now turn to a class in which little regard has been paid to the gustatory organs, the sole object being to combine with the oil such substances as are likely to endow it with supplementary or increased efficiency. The value of these additions is always great—according to their inventors—but the preparations themselves are, as a rule, far from nice, and the poor patient is left to overcome his aversion to swallowing them as best he can.

In some of the preparations the utmost ingenuity has been brought into play in order to combine cod-liver oil, a body with a most delicate and sensitive constitution, with some of her bitterest enemies, in a chemical sense. If emulsionists condemned the oil to life-long servitude, the improvers upon them may certainly be said to have issued its death-warrant.

Iron is the chief factor that has secured the attention of workers in this field; and no pains have been spared to obtain a properly constituted *oleum morrhuæ ferratum.* A method for preparing an oil with a constant percentage of iron seems to have been successfully devised. But what an oil! In spite of assurances to the contrary—always emanating from the inventors of these preparations—we doubt if many persons could be persuaded to take them, except, of course, little children, with whom persuasions of a certain kind are generally followed by satisfactory results.

We shall now give a short survey of the efforts made in order to obtain a reliable *oleum morrhuæ ferratum.* The first attempt was made as far back as 1861, but it was a comparatively tame one. Jeannel gave the following suggestion: 250 parts of oil are mixed with 14 parts of sodium carbonate, 14 parts of ferrous sulphate, dissolved in 250 parts of water, shaking occasionally for a week, and then filtering (*Rep. de pharm.*).

An improvement upon this, is to prepare first ferrous carbonate from ferrous sulphate by sodium carbonate, and then dissolve the precipitate in the oil heated on a water-bath (*Pharm. Centralhalle*, ii. 369).

Three years later the same journal proposes to dissolve ferrous stearate in the oil, but admits that it does not dissolve perfectly.

Two years afterwards C. Waeber, in *Pharm. Zeitsch. für Rusland*, 1866, recommended ferrous oleate in preference to stearate because it dissolves in all proportions.

In 1866 Ricker (*N. Jahrb. d. Pharm.*) recommended the preparation of an iron soap from the fatty acids of cod-liver oil by saponification with caustic soda, dissolving the soap in water and precipitating with ferrous sulphate. The precipitated iron soap is then dissolved in the oil.

The percentage of iron in all these preparations is variable, and in order to obtain an oil with constant percentage Stromeyer (*Arch. d. Ph.* xv.) devised the following method: 20 grms. of Castile soap are dissolved in 800 grms. of water; to the solution are added 7·5 grms. of a solution of ferric chloride (15 per cent.); 16 grms. of the iron soap thus formed are mixed with 84 grms. of cod-liver oil, the whole being gently heated. The preparation contains 1 per cent. of iron.

Such a discovery proved quite a stimulus to emulous pharmacists, and from Germany, France, and Holland there came in quick succession reports of still greater discoveries. Thus Schwartz (*Ph. Zeitg.* liii.) recommends iron benzoate in making ol. morrh. ferr. He dissolves 60 grms. toluyl-benzoic acid in 300 grms. water, adding 102 grms. liquor ammoniæ (10 per cent.); a mixture of 100 grms. Tr. ferri perchloridi and 300 grms. water is added, and the precipitate washed and dried: 20 grms. of this iron benzoate is triturated with 5 grms. toluyl-benzoic acid and some cod-liver oil, mixed with 1 kilo. more oil, and heated on a water-bath for an hour. It contains 2 per cent. ferric benzoate, or 0·3 per cent. metallic iron.

Godin, Paris, had a similar happy idea—dissolved 1 per cent. ferric benzoate in the oil. The preparation must, however, not be exposed to light, otherwise 'it assumes a rather unpleasant taste.'

Van der Burg (*Ph. Ztg.* 1881) prepares an iron-oil in this way:—Pour 3·5 parts of caustic soda solution into 100 parts of oil, heating on a water-bath, add 2 parts of ferrous sulphate, passing a current of air through the mass and keeping the temperature up to 90°. A compound is thus obtained which is quite clear, of a dark garnet-red colour, contains 0·25 per cent. iron, and 'has an unpleasant taste and smell.' It is therefore recommended to dilute it with—cod-liver oil.

Van Valkenburg's method of preparing an oil with iodide of iron:—Iodine, 1·25 parts, and cod-liver oil, 98·50 parts, are shaken up for some days until the iodine is dissolved, then 2·50 parts of iron are added, and the whole shaken occasionally until there is no reaction of free iodine.

Dietrich (*Neues ph. Manual*) gives, as late as 1886, two prescriptions for preparing oleum morrh. ferr., proving that this hapless preparation still haunts the pharmaceutical brain. One is identical with Godin's formula, the other is similar to Stromeyer's, both referred to above.

OLEUM MORRHUÆ OZONISATUM: a French remedy prepared by leading ozone through the oil!!

OLEUM MORRHUÆ CHLORALISATUM: cod-liver oil 190 parts and chloral hydrate 10 parts.

OLEUM MORRHUÆ CUM CREASOTO: cod-liver oil 4 fl. oz., creasote (beechwood) 100 minims, and saccharine 2 grains.

OLEUM MORRHUÆ CUM OLEO EUCALYPTI: 5 minims of eucalyptus oil to each drachm of cod-liver oil, made into an emulsion.

OLEUM MORRHUÆ ETHERISATUM, the only sensible preparation as yet suggested, was introduced by Dr. Foster, of Birmingham, and founded upon Claude Bernard's investigations on the mode of stimulating the secretion of the pancreas (vide *British Medical Journal*, Nov. 21 and 28, 1868). Dr. Foster recommended three degrees of strength to suit individual cases: 1, 3, or 5 minims of ether to 1 drachm of oil.

OLEUM MORRHUÆ PHOSPHORATUM: phosphorus 0·01 part dissolved in 100 parts of oil.

OLEUM MORRHUÆ PHOSPHORALE is a solution of 0·6 per cent. phosphorus in oil.

OLEUM MORRHUÆ SAPONIFICATUM: slaked lime 40 parts, water and oil each 100 parts, evaporated to the proper consistency for making pills.

PITJECOR is a mixture of cod-liver oil and catramin (*D. Med. Ztg.* 1890, p. 147).

## SUBSTITUTES

Substitutes for cod-liver oil have been brought more to the front by reason of the preparations just described. These have chiefly succeeded in rendering the oil perfectly horrible, while the substitutes are, at least, more palatable. They have, however, never met with extended sympathy amongst medical men, for many reasons. Their scientific vindication has been small to a degree, frequently incomprehensible, supported by mere postulates, without any confirmatory facts. A great many have been nothing more than pecuniary speculations, whose flicker has been fanned into flame by flourishing advertisements, and belong to the prolific class of patent medicines and proprietary articles. With the latter we shall not trouble the reader, but it may be interesting to recall some others which have attained a certain measure of favour.

The first substitute that we have come across is CREAM, which is recommended as an excellent substitute for cod-liver oil (*Bull. thérap.* 1863).

Next PORK-FAT (*Br. Med. J.* 1879), which is followed by a mixture of SPERMACETI 1 part and sugar 3 parts (*Monde pharm.*).

Then GLYCERIN, simple, is declared as good as the oil (*Ph. C.* v.), but has been superseded by GLYCERINUM TONICUM, which is composed of glycerin 300 grms., tinct. iodi 30 drops, and iodide of potassium 0·3 grm.

Several other oils have served as substitutes. SHARK-LIVER OIL from *Squalus uyatus* is by Italian practitioners considered quite equal to ordinary cod-liver oil, probably their constitutions are somewhat similar. EULACHON OIL, the fluid fat of *Thaleichthys pacificus*, the candle-fish found in the Pacific: this is, however, not liver oil, and has not its physical properties, being much more viscous. DUGONG OIL, which is said to some extent to substitute cod-liver oil in Australia, is the fat from the *halicore* or *dugong* (sea-cow), an herbivorous cetaceous animal belonging to the *Manatidæ*, and found in the Indian Ocean: this, again, is not a liver oil. JAPANESE COD-LIVER OIL is said to be derived from *Gadus Brandti*, a Japanese species of the cod. ALLIGATOR oil, CROCODILE oil, and TURTLE-EGG oil have also been used instead of cod-liver oil.

A milk decoction of the leaves of the GREAT MULLEIN (*Verbascum thapsum*) is reputed to have the weight-increasing properties of cod-liver oil, and is said to be much used in Ireland. 'It is superior in point of view of comfort to the patient' (Br. Pharm. Congress, 1883; vide *Ch. & D.* xxv. p. 500).

CREASOTE and GUAIACOL have been recommended as substitutes; but as they therapeutically belong to a class of materia medica widely different from cod-liver oil, it is difficult to see how the one can be substituted for the other. Creasote and guaiacol are supposed to destroy the tubercle bacillus, and consequently to *cure* the disease: the oil has no effect upon the bacillus, but provides materials for rebuilding the cells destroyed in the combat between them and the bacilli. Creasote and guaiacol may therefore be valuable adjuncts to the oil, but they cannot be substitutes for it.

There are several other preparations of the dietetic category. In these meat in one form or another forms the principal constituent, as meat-powder, meat-chocolate, etc. Besides these there is an imposing array of proprietary articles, the compositions of which are 'trade secrets,' and probably in most cases it would be inexpedient to declare the various ingredients, upon the principle that 'where ignorance is bliss, 'tis folly to be wise.'

### ACTIVE PRINCIPLES

Another class of substitutes enjoys a quasi-scientific origin resting upon the basis of the so-called 'active principle' of the oil.

The oldest of these active principles, iodine, was detected as one of the oil's constituents so far back as 1836 by Hopfer de l'Orme, and the percentage was variously stated to be from 0·0293 to 0·324 (100 to 1,000 times higher than the percentage, as since ascertained by more accurate modern methods). A most varied selection of iodine preparations as substitutes for the oil followed upon this discovery, the last example of which has already been mentioned as glycerinum tonicum, born 1871, died shortly after from consumption—or perhaps rather from too small consumption—*secundum legem talionis.*

When the iodine active principle was exploded another, trimethylamine, took its place, and as a result herring-brine, from being a rather neglected commodity, became for a short time the desideratum of the day.

After a quick succession of other active principles, too evanescent to be worthy of even an obituary notice, the turn came for the free fatty acids. No theory and no fact then supported the idea that these acids were the active principle in the oil; on the contrary, all observations tended to demonstrate that their presence was immaterial to its therapeutical value. Still, the belief entered some active mind (*Therap. Monatsh.* ii. 2) that they were the essential constituents, and that they might be fitly represented by oleïc acid, now proved conclusively not to be present in cod-liver oil. The new substitute was compounded from olive oil, to which was added 6 per cent of oleïc acid and given the name LIPANIN.

It had, like its brethren, a short life, though its great discovery was so enthusiastically received that one of the authorities recommended it as being, in addition to its therapeutic virtues, an excellent substitute for—*salad dressing.*

Lipanin was improved upon by a product, substituting lanolin for oleïc acid, and by another replacing olive oil by cacao-butter. The former was objected to by therapists (*Therap. Monatsh.* 1888, p. 3) because lanolin is not absorbable by the intestines. The latter, euphonised *invigorating chocolate* (Krafft-Chocolade), is compounded, it seems, by none other than the discoverer of lipanin: as it is still in the youthful stage we have no desire to cast its horoscope.

According to Marpmann (*Ph. C.* xxix. p. 406) pancreatic juice and cod-liver oil both contain an identical compound which easily emulsifies oil; it has, however, not been isolated, and is therefore merely hypothetical. But upon the hypothesis follows a theory, and upon this, of course a new substitute is compounded. The theory is as follows: cod-liver oil is therapeutically only a fat in the place of which any other fat will do equally well *if* mixed with the active principle, *i.e.*, the emulsifying agent referred to. This is found in pancreatic juice, and therefore olive oil digested with pancreatic juice is 'highly recommended as a substitute' for cod-liver oil.

Of course this was soon afterwards improved upon, by the addition of phosphate of calcium, alantol, alantic acid, and taurocholates, suggested by the American preparation hydroleïne, previously referred to. The new improved edition of digested olive oil has made its *début* as PINGUIN.

There are still two or three 'active principles' which have had, or still have, to serve as substitutes for cod-liver oil.

Despinoy and Garreau (according to *Zeitsch. d. allg. österr. Apoth. Vereins, Ph. C.*

v. 53) have found that the active principle of the oil is not in the oil at all, not even in the livers, but in the water squeezed out when the livers are macerated. This fluid contains a great percentage of ichthyoglycin (whatever that may be), chlorine, iodine, phosphoric acid, and propylamine. The product is made into pills which 'produce want of appetite and diarrhœa.' Nevertheless eight of them are equal to 360 grains of the oil on account of their favourable action on the nutrition!!

Meynet (according to *Neues Jahrbuch f. Pharmacie*, *Ph. C.* vi. 202) made dragées from the watery fluid of the livers, and a committee appointed by the authorities, at his instigation, to report upon the remedy stated that 'an analysis had disclosed *the fact* that the efficacy of 20 grammes of the extract was equal to that of 5 litres of cod-liver oil'!

Chapoteaut (*American Journ. Ph.* 1886) has isolated a body which he calls *morrhuol*, and which, he says, represents the active principle of cod-liver oil. It is prepared from the oil by first treating it at a low temperature with an aqueous solution of sodium carbonate and then shaking it with alcohol (90 per cent.). The alcoholic solution, separated and evaporated, leaves a residue which is morrhuol, a strongly smelling substance having a sharp and bitter taste: it partly solidifies at ordinary temperatures, and is said to contain iodine, bromine, and phosphorus. The discoverer computes 0·02 grm. to be equal to 5 grms. of oil.

Morrhuol is evidently identical with the ptomaïnes found in LIGHT-BROWN cod-liver oil by Gautier and Mourgues (*les alcaloïdes de l'huile de foie de morue*), viz., asseline, morrhuine dihydrolutidine, etc., and which were collectively termed *pangaduine* by Bouillot (*Compt. rend.* cxvi. 439). They are poisonous substances, probably analogous to if not identical with those found in putrid meat, poisonous cheese, etc.; and those should with the same right be considered the 'active principle' of cheese and meat, and used for the benefit of 'suffering humanity.'

WINE OF COD-LIVER OIL, so called, appears to be identical with a solution of morrhuol.

The real active principle of cod-liver oil will be discussed later in connection with Heyerdahl's researches and discoveries. We shall see how hopeless is this search after a substitute for cod-liver oil, for the simple reason that the main constituents of the oil are absolutely unique, and that its active principle is the oil itself.

# CHRONOLOGICAL SYNOPSIS OF CHEMICAL RESEARCHES ON COD-LIVER OIL

CONTRIBUTED BY P. M. HEYERDAHL

1822.—Wurzer (*Hufel. Journ.* Dec. 1822, p. 31). The first chemical examination of cod-liver oil was made by Wurzer in 1822. *Light brown oil* was shaken up with water, and the aqueous yellow extract, left on evaporation, was a viscous, yellowish substance, acid in reaction, smelling of herring, disgustingly bitter to the taste, deliquescent, and soluble in water and alcohol.

1828.—Spaarmann (*Geig. Mag.* June 1828, p. 302) examined *light brown oil.* With water he extracted 4·5 per cent. of a fishy-smelling substance, of an acid reaction, soluble in alcohol and precipitated by acetate of lead or infusion of galls. The oil was next dissolved in boiling alcohol, and after being cooled it separated into 19 parts stearin (margarin) and 76·5 parts oleïn. He saponified the oil with caustic potash solution and decomposed the soap with tartaric acid; the separated free fatty acids were then dissolved in boiling alcohol, from which, upon cooling, margaric acid crystallised. The mother liquor was distilled, and the acid distillate after being neutralised by baryta water was evaporated and decomposed by phosphoric acid, when delphinic acid separated; not free, however, from colouring impurities, and with the smell of herring brine. The delphinic acid was a brownish yellow oil, sp. gr. 0·941. One hundred parts of cod-liver oil yielded in this way—

| | | |
|---|---|---|
| 17 | parts of | margaric acid |
| 74·5 | „ | oleïc acid |
| 5·5 | „ | delphinic acid |
| 3·0 | „ | colouring and smelling matter |

1830.—Marder (*Brandes Archiv*, xxxii. 90; *Pharm. Centralbl.* 1830, p. 17; and *Hufel. Journ.* May 1837, p. 115) examined *brown and pale oils*, and found the constituents of the oils and their percentage to be:—

| | Pale oil | Brown oil |
|---|---|---|
| Green soft resin | 0·052 | 0·065 |
| Brown hard resin | 0·013 | 0·078 |
| Animal glue (gelatine) | 0·156 | 0·468 |
| Oleïc acid | 55·917 | 47·500 |
| Margaric acid | 10·312 | 4·000 |
| Glycerin | 8·416 | 9·000 |
| Colouring matter | 5·750 | 12·500 |
| Chloride of calcium | 0·052 | 0·105 |
| Chloride of sodium | 0·059 | 0·094 |
| Sulphate of potassium | 0·018 | 0·031 |

He found that pale oil exposed to a low temperature deposited a solid fat, consisting of oleïc acid, margaric acid, and glycerin, but brown oil did not; further, that the latter had a greater refractive index and a more acid reaction than the former. The pale oil viewed by transmitted light appeared yellow, but, by reflected light, green. Both were soluble in ether in all proportions. One hundred parts of alcohol, sp. gr. 0·825, dissolved at 77°·5 nine parts of pale oil and one hundred parts of brown oil. Water shaken with either oil acquired an acid reaction and a disgusting smell of train-oil. Both oils were saponifiable with ammonia; formed milky liquids with barium hydrate; were not affected by tincture of galls, nitrate of silver, nitrate of mercury, stannous chloride, or potassium ferro-cyanide. With large quantities of solution of subacetate of lead they formed a sort of liniment. By mixing with nitric acid no heat was evolved, but the acid altered the odour and deepened the colour. Sulphuric acid produced, with evolution of heat and formation of sulphur dioxide, a red colour turning into black, and made the oil more viscous. Solution of chlorine had no particular effect upon either of the oils.

1836.—Hopfer de l'Orme (*Hufel. Journ.* April 1836, p. 115) was the first to recognise the presence of *iodine* in light brown oil.

1838.—Wachenroder (*Arch. d. Ph.* xxiv. 145; *Centralbl.* 1841, p. 11) saponified the oil by boiling it for a considerable time with pure caustic potash in excess, evaporated the soap-solution to dryness, ignited the soap in a platinum crucible, adding a little ammonium carbonate towards the close, and finally extracted the soluble portion of the ash with water or alcohol. In the latter case, after evaporation of the alcohol, a fairly pure potassium iodide remained, which was dissolved in water and precipitated with nitrate of silver. The precipitate was treated with dilute nitric acid and subsequently with ammonia to remove the silver chloride, bromide, and carbonate, and it was then washed and dried. Brown oil yielded 0·324 per cent. of iodine in one case, and in another 0·162 per cent.

1839.—Herberger (*Ann. d. Ch.* xxxi. 94; *Jahrb. f. pr. Ph.* 1839, p. 178; *Centralbl.* 1839, p. 853) dissolved the salt, obtained by ignition, in water, precipitated the iodine with blue and green vitriol as cuprous iodide, filtered, evaporated, and distilled the residue with manganese peroxide and sulphuric acid, agitated the distillate with ether, and, after evaporation of the latter, determined the bromine as potassium bromide.

He obtained the following results :—

| | Iodine Per cent. | Bromine Per cent. |
|---|---|---|
| In pale oil . . | 0·0293–0·0903 | 0·0170 |
| ,, light brown oil . | 0·0375–0·1723 | 0·0294 |
| ,, brown oil . . | 0·0318–0·0412 | 0·0101 |

Herberger assumed that bromine was present in the form of magnesium bromide because magnesia was found in all samples containing bromine, but not in those destitute of bromine.

1840.—Stein (*Journ. f. pr. Ch.* xxi. 308) showed that the percentage of iodine could not be determined by simple extraction with alcohol, ether, or water, nor could it be done reliably by direct carbonisation of the oil and treatment of the carbon with solvents, but only by saponification of the oil with caustic potash or soda and ignition of the soap. Qualitatively the presence of iodine was best demonstrated by heating the aqueous or alcoholic extract of the ignited soap (evaporated to dryness) with concentrated sulphuric acid, when the fumes arising would react on starch.

1843.—De Jongh (*Disquisitio Comparativa Chemico-medica de Tribus Olei Jecoris Aselli Speciebus*) made an extensive examination of pale, light brown, and brown oil, of which the following is an extract.

*Physical Properties.*—The brown oil, *oleum jecoris aselli fuscum*, is of a dark-brown colour, greenish in refracted light, and transparent in thin layers; its smell is peculiar and unpleasant; its taste bitter, empyreumatic and caustic; reaction on litmus paper slightly acid; sp. gr. at 17½° 0·924. Cold alcohol dissolves from 5·9 to 6·5 per cent., boiling alcohol 6·5 to 6·9 per cent., and it is soluble in all proportions in ether.

The light-brown oil, *oleum jecoris aselli subfuscum*, is in colour like Malaga wine; smell peculiar, not unpleasant, but stronger, however, than that of pale oil; taste fishy, bitter, and burning in the throat. Slightly acid reaction; sp. gr. at 17½° 0·924. Cold alcohol dissolves from 2·8 to 3·2 per cent., hot alcohol from 6·5 to 6·8 per cent. Ether dissolves it in all proportions.

The pale oil, *oleum jecoris aselli flavum*, has a golden yellow colour; a smell peculiar, but not unpleasant; taste fishy, not bitter; reaction slightly acid; sp. gr. at 17½° 0·923. Cold alcohol dissolves from 2·5 to 2·7 per cent.; hot alcohol from 3·5 to 4·5 per cent., and it is dissolved by ether in all proportions.

*Organic Constituents.—Bilious Matters.*—The three oils were agitated with cold water, producing an emulsion from which the oil slowly separated. The brown oil caused the water to become discoloured and empyreumatic, while neither of the other oils discoloured it: in all three cases the water assumed a slightly acid reaction. The oils after the agitation were clearer, less strong in smell, and less acid in reaction.

Boiling the oil with water gave the same results. By evaporation of the aqueous extract a reddish-brown substance was obtained, which became softer on being heated, and was scarcely soluble in water, more so in ether, and entirely soluble in alcohol. Alkaline fluids dissolved this substance and acids precipitated it again in the form of a reddish-brown flaky deposit. The extracts had a peculiar smell and a bitter taste.

The amounts obtained from each of the three oils were as follows:—

| | With cold water<br>Per cent. | With hot water<br>Per cent. |
|---|---|---|
| Pale oil . . . . | 0·607 | 0·513 |
| Light brown oil . . | 0·890 | 0·849 |
| Brown oil . . . | 1·288 | 1·256 |

Subsequent treatment by ether, alcohol, and spirits gave like results with all of these extracts.

By ether there was obtained a reddish-brown, transparent, viscous extract which melted when heated, stained paper, and smelt and tasted like bile. After a time it formed small crystals. The extract was very sparingly soluble in water, but easily dissolved in alcohol or ether. A solution of ammonium carbonate added to a solution of the extract in ether produced two layers, the upper one being thick and turbid, and on evaporation separating drops of oleïn, some crystals of margarin, and a brownish substance which had a bitter taste, and proved identical with the substance obtained by evaporation of the lower or ethereal layer, which on treatment with water separated into a soluble and an insoluble part, and consisted of *ammonium fellinate* and *cholate*.

From that part of the extract which was insoluble in ether, alcohol dissolved a blackish-brown, odourless, bitter, glittering, hygroscopic mass, not easily soluble in water. It consisted of *bilifulvin*, *biliverdin*, and *bilifellic* acid.

Dilute alcohol extracted from the residue a black, glistening substance soluble in alkalis, concentrated sulphuric acid, and hot acetic acid, but insoluble in nitric and hydrochloric acids. Baryta water and lead acetate precipitated brown flakes in the alcoholic solution. No ash was left on incineration.

That part of the aqueous extract which remained after treatment with the above-named three solvents contained an *organic substance*, the nature of which was not determined, and *norganic salts*, among which were found *hydrochloric*, *phosphoric*, and *sulphuric acids*, *lime*, *magnesia*, and *soda*, but neither potassium nor iodine.

*Glycerin.*—This was prepared by saponification with caustic soda. The under-lye was drawn off and neutralised with sulphuric acid, and the sodium sulphate thus formed was separated by evaporation and crystallisation. The glycerin so obtained was found on comparison to be darker than that obtained from olive oil or from lard. All of them were decolourised by adding basic lead acetate to the aqueous solutions, but they turned brown again on heating.

Quantitatively the three oils contained glycerin as follows:—

| | | |
|---|---|---|
| Brown oil contained . . | 9·711 | per cent. glycerin |
| Light brown oil contained . | 9·073 | „ „ |
| Pale oil contained . . | 10·177 | „ „ |

*The Fatty Acids.*—The separation of the fatty acids was effected by decomposing the soda soap with lead acetate and digesting the lead soap with ether. The insoluble part was found to consist of *lead margarate* and the ethereal solution contained *lead oleate*. The quantitative determination gave the following results:—

| | Margaric acid<br>Per cent. | Impure oleïc acid<br>Per cent. |
|---|---|---|
| Brown oil contained . . | 16·145 | 69·785 |
| Light brown oil contained . | 15·421 | 71·757 |
| Pale oil contained . . | 11·757 | 74·033 |

*Gaduin.*—The ethereal solution of the lead soap from each of the three oils contained, besides lead oleate, a brown substance in each case identical. This was obtained by the following process.

The lead oleate was decomposed with sulphuric acid and the separated free oleïc acid saponified with sodium hydrate. After saponification the lye was almost black, containing the greater part of the brown substance. The soap was removed, the lye filtered and neutralised with sulphuric acid, when brownish-yellow flakes were formed rising to the surface. These were collected, washed with water, and dissolved in spirit; but after evaporation to dryness the substance was not again entirely soluble in spirit. The ultimate analysis, however, of the lead and silver salts—the substance appearing to have the character of an acid—and the analysis of the substance itself proved the soluble as well as the insoluble part to be the same compound, but in two modifications. The formula of this when dried at 110° was found to be $C_{39}H_{52}O_{12}$ (Berzelius' equivalents $C=75$, $H=6·25$, $O=100$), and when dried at 140° $C_{35}H_{46}O_9$; the difference $C_4H_6O_3$ being the elementary composition of 'anhydrous acetic acid,' which de Jongh considered as foreign to the compound, and as having its origin from the lead acetate used for the formation of the lead soap. He gave the brown substance the name of *gaduin*, and looked upon it as an hydrated oxide of an unknown hydrocarbon $C_5H_6$, its rational formula being $7\ (C_5H_6O)\ 2\ (H_2O)$. Of the two molecules of water, however, only one was replaceable by metallic oxides—according to the theories of 1843.

*Volatile Acids.*—These were prepared by saponification with caustic potash and decomposition of the soap with dilute sulphuric acid. The acid aqueous fluid, together with the wash-water from the fatty acids, was then distilled. The distillate had a peculiar odour. When saturated with baryta water and evaporated to dryness a part of it was soluble in alcohol, another part insoluble. The insoluble part was found to be *barium acetate* with two molecules of water of crystallisation. The soluble part was *barium butyrate.* Quantitatively there was found—

| | Butyric acid Per cent. | Acetic acid Per cent. |
|---|---|---|
| Brown oil . . . | 0·15875 | 0·12506 |
| Pale „ . . . | 0·07436 | 0·04571 |

The percentage in light brown oil was about the same as in the pale oil.

*Inorganic Constituents.—Iodine.*—De Jongh corroborated Stein's observation that iodine cannot be detected and determinated by incineration of the oil or by saponification and subsequent decomposition with acids, but only by the saponification and incineration of the soap. Consequently iodine is not present in the oil either in the free state or as a metallic iodide, but probably as some organic combination.

The quantitative estimation was effected by Lassaigne's method, by which a perfectly neutral solution of the iodine compound is precipitated by a perfectly neutral solution of palladium nitrate. The oil was saponified with caustic potash in an iron crucible, the soap incinerated, and after cooling extracted with absolute alcohol. The extract was evaporated, the residue dissolved in water, the alkaline solution carefully neutralised with dilute sulphuric acid and precipitated with palladium nitrate, the sediment filtered off, washed, and dried at 100°.

| | Iodine Per cent. |
|---|---|
| Brown oil was found to contain . . | 0·0295 |
| Light brown oil was found to contain . | 0·0406 |
| Pale oil was found to contain . . . | 0·0374 |

*Bromine.*—The presence of bromine was demonstrated by Balard's method. The oil was saponified with caustic potash, the soap incinerated and extracted with alcohol; the alcoholic extract evaporated, the residue dissolved in water, filtered, and treated with chlorine. This solution was then agitated with ether, which assumed a brownish colour, but was decolourised again on treatment with caustic potash solution. The solution was evaporated to dryness, moistened with sulphuric acid, and heated in a retort; iodine fumes were evolved and also distinct fumes of *bromine* which coloured the water first condensed in the receiver brown. All oils gave the same result, but the amount of bromine was too small to be quantitatively determined.

*Chlorine.*—The incinerated potash soap was extracted with hot water, the aqueous solution concentrated, acidulated with nitric acid, and precipitated with nitrate of silver, the sediment filtered off, washed, and dried. In the quantitative determination allowance was made for the calculated amount of iodide of silver, the rest being *chloride* and *bromide* of silver, the amount of the latter being insignificant.

| | Chlorine, incl. bromine Per cent. |
|---|---|
| Brown oil contained . . . | 0·0840 |
| Light brown oil contained . . | 0·1588 |
| Pale oil contained . . . . | 0·1488 |

*Phosphoric and Sulphuric Acids.*—The oil was saponified with caustic potash, the soap decomposed with hydrochloric acid, the fatty acids removed, and the *phosphoric acid* precipitated with ferric nitrate and ammonia in excess. *Sulphuric* acid was precipitated from the solution with barium nitrate.

| | Phosphoric acid Per cent. | | Sulphuric acid Per cent. |
|---|---|---|---|
| Brown oil was found to contain. . . . | 0·05365 | and | 0·01010 |
| Light brown oil was found to contain . . . | 0·07890 | „ | 0·08595 |
| Pale oil was found to contain . . . . | 0·09135 | „ | 0·07100 |

*Phosphorus and Sulphur.*—In order to determine whether phosphorus and sulphur were present in cod-liver oil, either in a free state or in an organic combination, a certain quantity of the oil was oxidised with concentrated nitric acid and the amount of phosphoric and sulphuric acids in the oxidised fluid determined by the above method. More phosphoric acid was found in the oxidised oil than in the non-oxidised, the difference denoting the amount of free phosphorus in the oil.

| | | |
|---|---|---|
| Brown oil contained . | 0·00754 % | of such phosphorus |
| Light brown oil contained | 0·01135 „ | „ |
| Pale oil contained . | 0·02125 „ | „ |

*Lime, Magnesia, and Soda*—These were determined by incineration of the oil and extraction with hydrochloric acid. The phosphoric acid was precipitated with ferric nitrate and ammonia, and the precipitate filtered off and washed. The filtrate and wash-water were precipitated with ammonium oxalate, and the *calcium* oxalate formed was filtered and determined. *Magnesia* was precipitated from the filtrate with ammonium phosphate, and to the filtrate from this, ferric nitrate and ammonia were added, precipitating the phosphoric acid. This was removed by filtering, the filtrate acidulated with sulphuric acid, evaporated to dryness, and incinerated, whereupon the percentage of soda was determined. Potassium and iron were not present.

| — | Calcium oxide | Magnesia | Sodium oxide |
|---|---|---|---|
| | % | % | % |
| Brown oil contained. . | 0·0817 | 0·0038 | 0·0179 |
| Light brown oil contained | 0·1678 | 0·0123 | 0·0681 |
| Pale oil contained . . | 0·1515 | 0·0088 | 0·0554 |

TABULATED ANALYSIS

| — | Brown oil | Light brown oil | Pale oil |
|---|---|---|---|
| Oleïc acid with brown substance (gaduin and two peculiar compounds) . . | 69·78500 | 71·75700 | 74·03300 |
| Margaric acid . . . . | 16·14500 | 15·42100 | 11·75700 |
| Glycerin . . . . . | 9·71100 | 9·07300 | 10·17700 |
| Acetic acid . . . . | 0·12506 | | 0·04571 |
| Butyric acid . . . . | 0·15875 | | 0·07436 |
| Fellic and cholic acids, together with undissolved oleïn, margarin, and bilifulvin . . . . . | 0·29900 | 0·06200 | 0·04300 |
| Bilifulvin, bilifellic acid, and two peculiar substances . | 0·87600 | 0·44500 | 0·26800 |
| A peculiar substance soluble in alcohol 30° . . . | 0·03800 | 0·01300 | 0·00600 |
| A peculiar substance insoluble in water, alcohol, and ether . . . . | 0·00500 | 0·00200 | 0·00100 |
| Iodine . . . . . . | 0·02950 | 0·04060 | 0·03740 |
| Chlorine with some bromine . | 0·08400 | 0·15880 | 0·14880 |
| Phosphoric acid . . . | 0·05365 | 0·07890 | 0·09135 |
| Sulphuric acid . . . | 0·01010 | 0·08595 | 0·07100 |
| Phosphorus . . . . | 0·00754 | 0·01136 | 0·02125 |
| Calcium oxide . . . . | 0·08170 | 0·16780 | 0·15150 |
| Magnesia . . . . . | 0·00380 | 0·01230 | 0·00880 |
| Sodium oxide . . . . | 0·01790 | 0·06810 | 0·05540 |
| Iron . . . . . . | traces | | |
| Loss . . . . . . | 2·56700 | 2·60319 | 3·00943 |
| | 100·00000 | 100·00000 | 100·00000 |

De Jongh supposes that Marder's green soft resin is a mixture of bile-constituents, some oleïn, and margarin, and that the hard resin soluble in alcohol consists principally of bilifulvin and bilifellic acid.

1851. — Personne (*Mémoire présentée à l'Académie Nationale de Médecine*, 1851), like de Jongh, found more iodine in the light brown than in the pale oil. He supposed the element to be present in the liver as potassium iodide, and to be set free by the joint action of air and fatty acids (produced by a partial decomposition of the oil). It then acted upon the fat by substituting the hydrogens in the same way as chlorine or bromine. He found *no trace of phosphorus.* Oil in which this element has been found must have contained liver parenchyma in suspension, this being the source of the calcium phosphate found.

1852.—Riegel (*Arch. d. Pharm.* cxx. 48; *Jahresb. d. Chemie*, 1852, p. 707) tested *pale, light-brown*, and *brown oil* for *sulphur*, *phosphorus*, *iodine*, *bromine*, *chlorine*, *sulphuric* and *phosphoric acids.* The following percentages were obtained:—

| — | Brown oil | Light brown oil | Pale oil |
|---|---|---|---|
| Sulphur . . . . | 0·0160 | 0·0180 | 0·0200 |
| Phosphorus . . . | 0·0090 | 0·0140 | 0·0205 |
| Iodine . . . . | 0·0350 | 0·0405 | 0·0327 |
| Bromine . . . . | 0·0037 | 0·0048 | 0·0045 |
| Chlorine . . . . | 0·1020 | 0·1133 | 0·1120 |
| Sulphuric acid . . . | 0·0475 | 0·0690 | 0·0640 |
| Phosphoric acid . . | 0·0632 | 0·0753 | 0·0710 |

1853.—Winckler (*Arch. d. Ph.* cxxvi. 185) inferred from his researches that by saponification of the oil oleïc and margaric acids and *propyl oxide* were formed, but *not glycerin.* By distilling the soap with a solution of caustic potash he obtained *ammonia* and a trace of *trimethylamine.*

1856.—Luck (*Jahresb. d. Chemie*, 1856, p. 490) found that cod-liver oil on being warmed, and subsequently cooled to 5°, deposited a sediment consisting of small crystalline flakes of a fatty acid. This he purified by saponification, precipitation of the aqueous solution of the soda-soap with lead acetate, washing the dried precipitate with ether, decomposition of the residue with hydrochloric acid, and recrystallisation from alcohol of the fatty acid thus obtained.

This acid had m.p. between 63° and 64°, and remained plainly crystalline at 60°. He gave it the name of *gadinic acid*, and by the ultimate analysis of its barium and silver salts found its empirical formula to be $C_{29}H_{28}O_3$. The discoverer took this to be the solid fatty acid in cod-liver oil.

Berzelius (Pereira: *Elements of Materia Medica*, ii. 779) was struck by the analogy between the reactions of de Jongh's gaduin and bilifulvic acid, and was inclined to suppose that gaduin was originally bilifulvic acid, and that the reddish-brown substance insoluble in alcohol and in water which he (Berzelius) prepared from bilifulvin by numerous and protracted operations was nothing but the insoluble modification of gaduin.

1862.—Nadler (*Jahresb. d. Chemie*, 1862, p. 64) determined the percentage of iodine in various oils, and found that light-brown oil contained least, water-white (probably steam-prepared) oil somewhat more, and de Jongh's oil (light brown oil) most iodine. The first two varieties contained iodine as a component of the fatty acids, while in the latter it was present both in the soap and in the under-lye.

1865.—Oswald Naumann (*Arch. d. Heilkunde*, 1865) found that cod-liver oil dialysed quicker, rose higher in capillary tubes, was more easily oxidised than neat's-foot oil, and he showed by experiments made on living cats that it was 1·8 times more readily absorbed.

1869. — Carl Schaper (Wiggers, *Hufem. Jahresb. d. Ph.* 1869, p. 340) examined Labrador oil. It was of a pale wine-yellow colour, had a peculiar odour of fish, sp. gr. 0·9219 at 8°, was perfectly clear at 15°, deposited a solid fat at 6°, and at −2° solidified to a thick oleaginous mass. It was neutral to test-paper, but slowly exhaled a minute quantity of a volatile fatty acid which coloured litmus-paper a wine-red. The oil was soluble in all proportions in ether, but only slightly in alcohol. Heated with a solution of caustic soda it gave off a faint but distinct smell of *trimethylamine* and subsequently of *ammonia.* The soap thus formed was treated with sulphuric acid, the fatty acids removed, and the under-lye heated, when, first the smell of *acetic acid* was distinctly recognisable, and then that of *butyric acid*: about 10 per cent. of glycerin ($C_6H_{16}O_6$ corresponding to 7 per cent. lipyloxide, $C_6H_{10}O_3$; compare analysis below) was obtained. The fatty acids formed a yellowish, soft, butter-like mass, still smelling of fish. The component parts were by analysis found to be palmitic and elaïc (oleïc) acids only, in the proportion of 1 : 2·7; the palmitic acid contained a little stearic acid. Schaper tabulated the percentage of constituents of the fatty acid mass as follows:—

| | |
|---|---|
| Palmitic acid . . . . . | 25·511 |
| Elaïc acid . . . . . . | 68·574 |
| Lipyloxide ($C_6H_{10}O_3$) . . . | 5·915 |
| | 100·000 |

From this result Schaper concludes that cod-liver oil is a mixture of palmitin and elaïn (oleïn).

He points out that the oil on treatment with concentrated sulphuric acid turned a beautiful purple, and later a brown, from which he inferred the presence of *biliary matter*, but did not extend his examinations farther. On the other hand, he found the percentage of iodine to be 0·015, and that of chlorine 0·0016.

1880.—Maumené (*Compt. rend.* xcii. 721) found that drying oils when mixed with sulphuric acid evolved a greater quantity of heat than other oils, and also that the maximum temperature for each oil was always the same when the experiments were carried out under the same conditions. He mixed 10 c.cm. of conc. sulphuric acid with 50 grammes of oil, stirring quickly with a thermometer until the mercury began to fall. The difference between the original and the highest temperature was the measure of heat evolved.

For steam-prepared oil the difference was found to be 103°
„ brown oil „ „ „ 89°·5

1882.—P. Carles (*Ph. Centralh.* xxiii. 279; *Journ. de Ph. et Ch.* v. 145) demonstrated experimentally that the phosphates are present in solution and not in suspension, and that the percentage is greater the darker and more acid the oil is. On the other hand, a freshly prepared, filtered, and neutral oil does not contain even a trace of phosphorus compounds. For his experiments he employed absolutely neutral, fresh, and filtered oil; liver parenchyma from which all fat had been removed by pressure and boiling; and the free fatty acids obtained from the potash soap of the same pure oil by decomposition with hydrochloric acid.

One hundred grains of oil and 7 gr. of parenchyma were introduced into one flask; 10 gr. of oil, 7 gr. of parenchyma, and 10 gr. of fatty acids into another; and the same quantities with 20 gr. fatty acids into a third flask. After being allowed to digest on a hot water-bath for several hours, each sample was filtered separately and decomposed by *aqua regia* poor in hydrochloric acid; and the phosphoric acid in the residue was then titrated with a solution of uranium.

In the first case no trace of phosphorus was found
„ second case 0·0022 gr. „ „
„ third „ 0·0074 „ „ „

From these results Carles infers that the percentage of phosphorus in the brown varieties of the oil is dependent on the amount of acid which they contain, because the phosphates of the tissue have been dissolved in proportion to the amount of acid contained.

Starting from the observation that no *iodine* is found in fresh oil, while it is present in the acid brown oil in proportion to its colour and acidity, the author concludes that the cause of its presence is the same as that of phosphorus. In the fermentation process formerly in use, the livers were exposed to the air, and the higher temperature thereby created caused the oil to absorb oxygen in the form of ozone, which is capable of isolating iodine from the alkaline earths contained in the liver parenchyma. It is this iodine which in the nascent state combines with the fatty compounds.

Carles maintains that neutral filtered oils are entirely free from phosphorus and iodine; when other investigators such as Graeger, Wackenroder, de Jongh, and Mitch. Bird (*Ph. Journ.* February 1882) have found iodine, it must be supposed that they have had less pure material for their experiments, or else that the potash they employed was not free from iodine.

1883.—Schädler (*Technolog. d. Fette*, 2nd ed. i. 773) recommended the solubility of cod-liver oil in boiling alcohol as a means of distinguishing it from other oils. In 100 parts of alcohol there are soluble 4 parts of cod oil, 7 parts of cod-liver oil, 15 parts of seal oil, and upwards of 100 parts of whale oil. But eventually great differences were found in the solubility of cod-liver oil.

Stanford (Br. Pharm. Conference, 1883; *Ph. Journ. and Trans.* No. 679, p. 353).—Most of the published analyses of cod-liver oil are much too high in the amount of iodine found. Six specimens were examined by the method used for kelp. The results were as follows:—

| | Percentage of iodine |
|---|---|
| Pale cod-liver oil . . . . | 0·000410 |
| Norwegian oil . . . . | 0·000434 |
| Scotch oil . . . . . | 0·000276 |
| English oil . . . . . | 0·000138 |
| Newfoundland oil . . . | 0·000315 |
| Light-brown oil . . . . | 0·000360 |

Herrings contain four times the amount of iodine found in cod-fish.

1884.—Kremel (*Ph. Centralh.* xxv. 337) studied cod-liver oil with a view to determining characteristic marks of distinction between cod-liver oil, Japanese oil, coal-fish oil, and seal oil. He has tabulated the results obtained as follows:—

| | — | Sp. gr. | Per cent. of fluid fatty acids | Per cent. of solid fatty acids | M.p. of solid fats | Acid value | Saponific value | Iodine absorption |
|---|---|---|---|---|---|---|---|---|
| 1 | Cod-liver oil, 1884 . . . . . . | | — | — | — | 0·62 | 171 | 131 |
| 2 | Cod-liver oil, 1883 . . . . . | 0·922 to 0·927 | 92·12 | 6·72 | — | 1·41 | 171 | 127 |
| 3 | | | — | — | — | 2·06 | — | 126 |
| 4 | | | 88·88 | 7·55 | 50°·5 | 2·23 | 189 | 127 |
| 5 | | | — | — | — | 2·32 | — | 128 |
| 6 | | | 90·46 | 6·88 | 51° | 2·86 | 179 | 131 |
| 7 | Cod-liver oil about 5 years old . . . | | — | — | — | 1·47 | 178 | 140 |
| 8 | Cod-liver oil about 10 years old, in badly corked bottles . . . . . . . | | — | — | — | 28·67 | — | — |
| 9 | Cod-liver oil about 10 years old . . . | | — | — | — | 5·03 | — | 129 |
| 10 | Pale cod-liver oil, 1883–84 . . . . | | — | 9·60 | 48–49° | 9·59 | 173 | 139 |
| 11 | | | — | — | — | 11·29 | 174 | 138 |
| 12 | | | — | — | — | 11·57 | 173 | 141 |
| 13 | | | 92·72 | 5·25 | 52° | 8·66 | 181 | — |
| 14 | | | 87·00 | 12·75 | 51–52° | 6·78 | 181 | 135 |
| 15 | | | — | — | — | 10·46 | — | 136 |
| 16 | Coal-fish-liver oil, 1883 . . . . | 0·925 | 75·32 | 19·04 | 55–56° | 1·26 | 177 | 137 |
| 17 | | 0·926 | — | 12·22 | 53° | 1·23 | 177 | 137 |
| 18 | | — | — | — | — | 1·29 | 179 | 129 |
| 19 | | 0·925 | 74·20 | 20·60 | — | 1·49 | 181 | 126 |
| 20 | | 0·927 | 70·00 | 21·34 | 52° | 1·68 | 181 | 123 |
| 21 | Japanese (cod ?) liver oil . . . . | 0·908 | 87·60 | 10·52 | 50–51° | — | — | 120 |
| 22 | Seal oil, 1883 . . . . . . | 0·925 | 85·02 | 10·23 | 57°·5 | 1·95 | 178 | 127 |
| 23 | | 0·925 | 88·29 | 9·81 | 57° | 2·01 | 179 | 128 |

The determination of solid and fluid fatty acids was carried out in the following manner:—The oil was saponified in alcoholic solution with caustic potash on a water-bath, neutralised with acetic acid, the alcohol evaporated, the soap dissolved in water and decomposed with a solution of subacetate of lead. The lead-soap washed with hot water and dried on a water-bath was separated by ether into a soluble and an insoluble part. The soluble plumbic salt contained the fluid, and the insoluble salt contained the solid fatty acids.

In order to determine the amount of free fatty acids (the acid-value or the number of milligrammes of KOH necessary to neutralise one gramme of fat) the oil was dissolved in ether and titrated with an alcoholic solution of potassium hydrate with phenolphthaleïn as indicator. Kremel found that a greater acidity was not attributable to rancidity, as the samples were all that could be desired in regard to this. He supposed that the acidity was dependent upon different methods of preparation.

The saponification value, *i.e.* the quantity of KOH in milligrammes necessary for the saponification of one gramme of fat, was determined by Köttstorfer's method—a weighed quantity of fat is saponified over a water-bath with a titrated alcoholic solution of potassium hydrate in excess, and the excess is retitrated with a titrated solution of hydrochloric acid.

The iodine absorption, *i.e.* the percentage of iodine which a fat absorbs, was determined by v. Hübl's method—a certain quantity of oil dissolved in chloroform was set aside for two or three hours with v. Hübl's iodine solution, and then the mixture was titrated with sodium thiosulphate. v. Hübl's iodine solution consists of 25 grms. of iodine and 30 grms. of mercuric chloride dissolved in one litre of 95 per cent. alcohol, the amount of iodine being accurately determined by sodium thiosulphate.

Kremel examined the behaviour of different oils towards fuming nitric acid by adding three to five drops of the acid to ten to fifteen drops of oil.

*Steam-prepared oil and pale oil* turn red at the point of contact, and upon being stirred rose-red; after a little while, however, this colour changes to a lemon-yellow.

*Coal-fish-liver oil* turns blue at the place of contact, and becomes brown on being stirred. The colour is retained for two or three hours, and then turns into a more or less pure yellow.

*Japanese oil* behaves in a similar way, save that some streaks of red appear beside the blue colour.

All these varieties give Pettenkofer's bile-reaction, turning purple when treated with concentrated sulphuric acid.

*Seal oil* was not affected by the addition of fuming nitric acid at first, but after a considerable time it turned brown.

Kremel found the reaction with fuming nitric acid so characteristic that by its aid he was enabled to detect an addition to cod-liver oil of 25 per cent. of any of the above-named oils.

Rössler (*Drogisten Zeitung*, 1884, No. 10) agitated cod-liver oil with concentrated *aqua regia*, forming a dark greenish yellow unctuous mass which in half an hour turned brown and remained so. Seal oil assumed a pale yellow colour.

1885.—Jean (*Monit. Scientif.* 1885, p. 892) found that 6 per cent. of the oil consisted of a light yellow oily unsaponifiable substance which is coloured brilliantly red by a drop of sulphuric acid. He also examined the increase in weight of cod-liver oil when exposed to dry air over sulphuric acid, and found that after three days it had increased 6·383 per cent.

Allen and Thomson (from Benedikt's *Analyse d. Fette*, 2nd edition, 369, shortly mentioned in *Allen's Analysis*) pointed out that cod-liver oil contains from 0·46 to 1·32 per cent. of cholesterin, obtained by saponification of the oil and extraction of the soap with ether. Recrystallisation from alcohol of the substance soluble in ether produced the characteristic plates of cholesterin.

Hager (*Ph. Centralh.* xxvi. 13) has made researches as to the detection of adulterations in cod-liver oil, and found the following tests sufficient.

When vigorously shaken with litmus tincture, steam-prepared oil of the best quality should retain the blue colour for at least an hour; slightly inferior or the best kinds of yellow oil show the red colour within ten minutes, while still more inferior oils colour red immediately.

*The Reaction with Concentrated Sulphuric Acid.*—Eight to ten drops of the oil are dissolved in 2 c.cm. of chloroform, and two drops of the sulphuric acid are added. The mixture when agitated assumes a light violet colour, immediately darkening and changing into a permanganate red, brownish red, dark brown, and finally blackish brown.

When one volume of the acid and two volumes of the oil are shaken up and allowed to stand for three or four hours a dark and rather stiff, unctuous mass is formed. If other fish oils are present the consistency of this mass is less firm and somewhat like vaselin.

The elaïdin test with nitric acid, sp. gr. 1·185, and a few copper filings invariably gives the same result—with genuine oil. No special change is noticeable in colour, nor is any deposit formed even after being kept for two or three days at a temperature of 7°–10°. A layer of elaïdin is yellow with a reddish-brown tinge, clear or slightly turbid, and less viscous than cod-liver oil. Separations in the oily layer denote the presence of foreign fats. Saponification of the oil is effected by mixing 7·5 grms. of the oil with 15 c.cm. caustic soda solution, sp. gr. 1·160, and 5 c.cm. water, slightly boiling four or five times, while constantly agitating the mixture. The saponification, however, is not complete, and therefore when the soap mixture has been set aside, first in a warm place for some hours, and then in a cold place, the mass will be found to consist of two layers, the top one being whitish and stiff, and the lower, transparent. The latter forms the larger part, and is the almost colourless fluid oil-like soap. Where foreign oils or resins are present this layer is merely translucent and not fluid. Adulteration with vaselin can be detected by the specific gravity, that of the oil varying between 0·920 and 0·930, usually from 0·922 to 0·925. To the practical chemist the squeaking sound produced by turning the cork moistened with oil in the neck of the bottle will betray the presence of mineral oils. To demonstrate chemically the presence of these oils is a difficult matter.

Boudard's nitric acid test is not reliable if the oil contains less than 15 per cent. of foreign fish fats. From 15 to 20 drops of nitric acid (sp. gr. 1·480–1·500) are added to 2 c.cm. oil, whereupon genuine oil gradually assumes a carmine colour.

An adulteration with resin will increase the specific gravity, and on saponification of such an oil the soap layer will be turbid and not transparent. The resin might be extracted from the oil by boiling and agitating it with dilute alcohol.

The presence of lead, which may arise from neutralisation of the oil with lead oxide, may be detected by extraction with dilute acetic acid, and neutralisation and precipitation with sulphuretted hydrogen.

1887.—Salkowsky (*Zeitsch. f. anal. Chemie*, xxvi. 1887) examined several methods intended to distinguish liver oils from vegetable oils.

*Determination of Solidifying and Melting Points.*—The temperature at which cod-liver oil solidifies was found to be rather low, but the several varieties, all undoubtedly pure oils, differed very much in this respect. While some remained fluid even at −15° others solidified at 0°. The melting point of congealed oil also varied considerably, being in five cases at or above 0° and in six others below 0°. Moreover it was found that the time of exposure had a great influence on the solidifying point: one sample stated to be non-congealing at −15° remained for some little time clear at that temperature, but solidified thoroughly at −4° if kept at that temperature for hours. In spite of these irregularities it was possible when the oil rapidly solidified at 0° to detect an admixture of 20 per cent. of palm oil, cocoa-nut oil, or palm-seed oil. Salkowsky believes that differences in the solidifying points of the oils arose from the fact that the fats which solidify at lower temperatures had been removed from some of the oils before they had been put on the market. All the samples congealed when exposed to a temperature of −10° to −12° for 2½ or 3 hours.

The Reichert-Meissl method has been devised to determine the saturation capacity of the volatile acids which may be contained in an oil. It consists in the alcoholic saponification of the oil with caustic potash, evaporation of the alcohol, solution of the soap in water, and decomposition by dilute sulphuric acid; 100 c.cm. are then distilled off and the distillate titrated with $\frac{1}{10}$ n. alkali solution.

Salkowsky found the requisite quantity of solution calculated for 5 grms. oil to be 0·10 to 0·20 c.cm. Other oils require perhaps a little more, except cocoa-nut and palm-seed oils, which require as much as 7·28 and 3·48 c.cm. respectively. These are the only two oils that can, therefore, with any degree of certainty be detected in cod-liver oil, and then, only provided they be present in considerable quantities. The reaction with cholesterin, phytosterin, and sulphuric acid was made in two different ways: by adding the acid direct to the oil; and by dissolving the oil in chloroform, adding the acid and shaking. The latter method is the better, as the colour is more stable. The mixture assumes first a violet colour, which is gradually changed into purple, reddish brown, and lastly dark brown. This remarkable and well-known reaction has been supposed to indicate the presence of biliary matters in cod-liver oil. Buchheim has, however, demonstrated that cod-liver oil does not contain any *biliary acids* or *bile pigments*, and, further, the chief pigment of the bile does not give the above reaction, nor is it to be detected in cod-liver oil. On the other hand this sulphuric acid reaction of the oil has some resemblance to that of cholesterin in choloroform solution.

In order to throw some light upon this matter the oil was saponified with an alcoholic solution of caustic potash, the alcohol evaporated, the soap dissolved in a large quantity of water, and the strongly alkaline solution shaken with ether. After separation and evaporation of the ether, a crystalline yellow substance remained which when recrystallised from alcohol formed a dazzling white crystalline mass of *cholesterin* with m.p. 146°. The solution in chloroform was colourless, and gave the typical reaction with sulphuric acid *without a trace of blue colour at the beginning of the reaction.* The percentage of cholesterin in the oil was found to average 0·3. The purple violet chloroform solution which floated upon the sulphuric acid became almost colourless or intense blue (*sic*) when diluted with more chloroform, but assumed the purple violet colour again upon being shaken. Salkowsky supposed this to arise from water contained in the chloroform.

The above-mentioned crystalline yellow substance left by the evaporation of the ether, dissolved, without application of heat, in chloroform, forming a perfectly clear golden yellow solution, which upon addition of sulphuric acid assumed a beautiful indigo blue colour, rapidly changing, however, into purple violet. Pure cholesterin, as it was obtained by the above-mentioned recrystallisation from alcohol, is never, like the yellow substance, coloured blue by sulphuric acid; consequently this yellow colour and the indigo blue reaction must be attributed to *the presence of a colouring matter*, which cannot be a bile pigment because it is not extracted from the chloroform solution by shaking it with a solution of sodium carbonate, but must belong to the class of *lipochromes* examined and studied by W. Kühne.

To the alkaline solution, obtained after the soap had been dissolved in water, the solution shaken with ether and ethereal extract of cholesterin and lipochrome removed, sulphuric acid was added in slight excess and the mixture again shaken with ether. After separation the ether was evaporated and the residue heated for some time on a water-bath. In this way the fatty acids were obtained. To a chloroform solution containing 5 to 8 per cent. of these acids an equal volume of sulphuric acid was added, when the latter was immediately coloured a deep brown, appearing dirty green in reflected light. Pouring off the colourless chloroform after the lapse of half an hour and adding a few drops of the sulphuric acid to some c.cm. of glacial acetic acid, the solution assumed after one or two hours a beautiful reddish violet colour with a dirty-green reflection, and maintained this colour for several days.

Thus cholesterin, lipochrome, and fatty acids are the constituents which play a part in the well-known colour reaction with sulphuric acid.

The only other pigment producing a blue colour with sulphuric acid was found in palm oil, and a trace of it in cotton-seed oil.

Salkowsky found that the cholesterin of cod-liver oil was not identical with that of the vegetable oils, the latter being much more like phytosterin as described by Hesse in 1878. Cholesterin forms a thickish mass of crystalline flakes, while phytosterin forms bushy groups of needles. Phytosterin, *slowly* crystallised, forms beautifully developed lengthy hexagonal plates, which is never the case with cholesterin. Phytosterin melts at 132°–134°, whereas the melting point of cholesterin is 146°. These differences are sufficiently characteristic for proving the presence of vegetable oils in cod-liver oil, the microscope being of great assistance in such examinations. Phytosterin dissolved in chloroform also gives a colour reaction with sulphuric acid, but the colour is more bluish than the cherry-red of cholesterin.

None of the fatty acids from vegetable oils when dissolved in chloroform behaved towards sulphuric acid and glacial acetic acid like the fatty acids of cod-liver oil as described above. Linseed and palm oil gave a faint indication of a similar behaviour.

Salkowsky, like Hager, found the free fatty acids were present in the better varieties of cod-liver oil, in only quite insignificant proportions, *i.e.* from 0·25 to 0·69 per cent.; in only one sample was there found as much as 6·5 per cent. Most vegetable oils contained larger quantities.

1888.—Van der Burg (*Encyclop. d. gesammt Ph.* 1889) found after incineration of the pale oil merely a trace of ash, not sufficient for determination by weight. In 22 grms. of de Jongh's oil he found 0·002 grm. of ash, containing calcium and iron.

Hirsch (*Encyclop. d. gesammt Ph.* 1889) gives the solubility of the light-coloured oils in cold alcohol as 1 in 40, in warm alcohol as 1 in 31–32 ; of the light brown oils in cold alcohol as 1 in 31–36, in warm alcohol 1 in 13, and of the brown oils in cold alcohol as 1 in 17–20.

In ether, cod-liver oil dissolved readily, *e.g.* in ether of sp. gr. 0·728 in less than twice its quantity ; in chloroform and carbon disulphide it also proved readily soluble.

Gautier and Mourgues (*Les Alcaloïdes de l'Huile de Foie de Morue*) examined the various cod-liver oils, and found in light-brown oil a small quantity of leucomaïnes, but not in the lighter oils.

One hundred kilos. of madeira-coloured (light-brown) oil was shaken with its own volume of alcohol (35 per cent.), containing 3 grms. of oxalic acid per litre. In order to prevent oxidation the air in the bottles employed in the process was replaced by carbonic acid. After standing for some time the alcoholic extract was drawn off and almost neutralised with milk of lime, after which it was filtered and distilled *in vacuo* at a temperature of 40°. When the liquid had been reduced to one-twentieth of its original volume, the distillation was discontinued ; the clear and slightly coloured liquid was saturated with calcium carbonate, filtered, and distilled *in vacuo* to dryness. The residue was treated with 80 per cent. alcohol, the extract filtered, the alcohol evaporated, and the liquid concentrated *in vacuo* to a syrupy fluid from which the bases were separated by the addition of dry potassium hydrate, and extracted by shaking with ether, from which they were precipitated by an ethereal solution of oxalic acid. The precipitate was washed with ether and dried. From 100 kilos. of oil 52 grms. of oxalates were obtained almost colourless and perfectly soluble in water. The bases were then isolated by dissolving the oxalates in a little water and adding potassium hydrate, when they appeared as a thickish brown floating layer, which was removed and dried over freshly fused potassium hydrate. Fifty-two grms. of oxalates gave 26·5 grms. of free bases. Subjected to fractional distillation, first under atmospheric pressure, afterwards under diminished pressure on an oil-bath, they separated into several volatile and non-volatile bases.

The first fraction which boiled at 87°–90° under a pressure of 770 mm. was *butylamine*, and constituted one-sixth of the whole. The ultimate analysis corresponded to the formula $C_4H_{11}N$.

The boiling point of the second fraction was between 94° and 100° under the same pressure (770 mm.). It consisted of *amylamine*, $C_5H_{13}N$, and constituted one-third of the whole.

The third fraction boiled under the same pressure between 100° and 115°, and proved to be *hexylamine*, $C_6H_{15}N$. It formed but an inconsiderable part of the constituents.

The fourth fraction boiled at 100° under a pressure of 60 mm., and at 198°–200° under 770 mm. pressure. It was *dihydrolutidine*, $C_7H_{11}N$, and constituted one-tenth part of the bases.

The residue from the distillation constituted the non-volatile bases. Treated with dilute hydrochloric acid and precipitated with platinous chloride, the precipitate was decomposed with sulphuretted hydrogen and again precipitated with caustic potash. Dried on unglazed tiles it was found to be *asseline*, $C_{25}H_{32}N$, and constituted barely one-fifteenth part of the bases.

The mother-lye from the platinum salt of asseline was evaporated, depositing a platinum salt from which, by decomposition at a higher temperature with sulphuretted hydrogen, there was obtained a chloride of *morrhuine.* The base morrhuine, $C_{19}H_{27}N_3$, was isolated with caustic potash, and by extraction with ether. It formed one-third part of all the bases.

After the bases had been extracted from the alkaline syrupy fluid by shaking with ether in the manner above described, the residue was examined in search of the acids with which the bases had probably been combined in the form of salts.

After adding a little sulphuric acid the following acids were obtained.

1. An acid which, especially on the application of heat, appeared as a brown sticky mass, capable, however, of crystallisation. It was a pyridine compound, and received the name of morrhuic acid, $C_9H_{13}NO_3$. One litre of oil contained one gramme of this body.

2. After the separation of morrhuic acid the liquid was distilled, and in the distillate were found formic and butyric acids.

3. In the residue there remained—

*a.* A small quantity of morrhuic acid, which was removed by alcoholic ether.

*b.* A certain quantity of phosphoric acid originating from phosphates, phosphorglycerins, and lecithins.

*c.* A little sulphuric acid of the same origin.

4. After the separation of these substances the remainder was precipitated with basic lead acetate, filtered, the lead removed with sulphuretted hydrogen, evaporated, and extracted with 98 per cent. alcohol. After the evaporation of the latter the liquid was distilled *in vacuo.* In the part of the distillate which boiled at 180° glycerin could be identified by its being converted into acroleïn.

1889.—Unger (*Südd. ph. Zeit.* 1888, p. 98, and 1889, p. 241) prepared three kinds of oil through putrefaction. The first oil drawn off from the livers had a light yellow colour, sp. gr. at 14° = 0·928; 1·69 per cent. free but not volatile acid; the second oil obtained from the same livers during the progress of putrefaction contained 4·78 per cent. free non-volatile acids;

the third oil was the last one obtainable, and was the darkest in colour. It contained 7·33 per cent. free acids (trace of propionic acid) and had a sp. gr. of 0·929. After standing for four hours in contact with nitric acid (sp. gr. 1·4) in a test-tube the first oil gave a cloudy ring of albuminates in combination with iron manganese and phosphorus; the other two gave no such reaction; still albuminous substances were present in them though in another form. The albuminous substances could be extracted from the oil by shaking with water in which they are soluble. Those extracted from the first oil smell of trimethylamine when boiled with water; the others do not. Unger concludes that the first oil is the only sort that should be employed as a medicine; about the second he is doubtful; the third oil he considers injurious.

The following researches on cod-liver oil are yet to be mentioned.

Grace Calvert's colour reactions (Benedikt's *Anal. d. Fette*, 2nd ed., p. 306).

| | sp. gr. | | | |
|---|---|---|---|---|
| Caustic soda . | 1·340 | colours | cod-liver oil | dark red |
| Sulphuric acid . | 1·475 | „ | „ | purple |
| „ „ . | 1·530 | „ | „ | „ |
| „ „ . | 1·635 | „ | „ | intense brown |
| Nitric acid . . | 1·180 | „ | „ | red |
| „ . . | 1·220 | „ | „ | pink |
| „ . . | 1·330 | „ | „ | red |
| Phosphoric acid . . | | „ | „ | dark red |
| Nitric acid mixed with sulphuric acid . . | | „ | „ | dark brown |
| *Aqua regia* . . . | | „ | „ | yellow |

Nitric acid of sp. gr. 1·33 and afterwards caustic soda of sp. gr. 1·34 form a fluid mass.

*Aqua regia* and afterwards caustic soda of sp. gr. 1·34 form a fluid orange-yellow mass.

Allen (Benedikt's *Anal. d. Fette*, 2nd ed., p. 368) found the saponification value of cod-liver oil to be 182–187.

Valenta found it to be 171–189.

Dieterich found the saponification value of the *acids* to be 204·4.

Chevallier and Baudrimont (König's *Analyse d. Nahrungs- und Genussmittel*) give the constituents of cod-liver oil as follows:—

| — | Oleïn | Margarin | Sulphur | Phosphorus | Iodine | Bromine | Chlorine | Sulphuric and phosphoric acids |
|---|---|---|---|---|---|---|---|---|
| White oil? (heller Leberthran) . . . . | 98·87 | 0·81 | 0·320 | 0·020 | 0·033 | 0·004 | 0·112 | — |
| Pale oil . . . . | 98·87 | 0·81 | 0·019 | 0·020 | 0·032 | 0·004 | 0·112 | 0·089 |
| Brown oil . . . | 98·80 | 0·93 | 0·016 | 0·019 | 0·031 | 0·003 | 0·102 | 0·092 |

1893.—Dr. W. Fahrion (*Chem. Ztg.* xxv. 434) assumes that the changes taking place in oils with high iodine absorption are caused by polymerisation. Unsaturated acids, on account of their double bonds, are strongly disposed to combine with other bodies, and when such are not present they will combine mutually. In the case of hydroxy-acids, however, the process is not a polymerisation but a condensation through the hydroxyls combining under elimination of water, leaving the double bonds undisturbed. As a consequence of such changes specific gravity, acid-value, and percentage of hydroxy-acids will increase, but iodine absorption will decrease. Thus he found the following changes to have taken place during the increasing age of a sardine oil:—

| — | Specific gravity | Iodine absorption | Acid-value | Hydroxy-acids |
|---|---|---|---|---|
| Original oil . | 0·933 | 193·2 | 20·6 | 0·6 |
| After six months | 0·936 | 179·7 | 25·3 | 1·1 |
| After a year . | 0·943 | 163·6 | 31·7 | 4·8 |

The free unsaturated acids must be considerably more disposed to polymerisation or condensation than their glycerides, and no reliable conclusions can, therefore, be drawn from the examination of their acid-value and iodine absorption; indeed the researches on the free fluid acids of the above-mentioned sardine oil proved the correctness of this assumption. Prepared at different times these acids gave the following values:—

| — | Iodine absorption | Acid-value | Molecular weight |
|---|---|---|---|
| I. | 229·4 | 189·4 | 295·7 |
| II. | 219·6 | 179·8 | 311·5 |
| III. | 198·0 | 174·7 | 320·6 |
| IV. | 74·4 | 100·0 | 560·0 |

The saponification value would naturally be expected to remain unaffected by the polymerisation and condensation processes which influence the other values so much. But even for this value no constant results could be obtained: they varied from 159·5 to 417·2, according to the time the alkali was allowed to act upon the free acids of the sardine oil. Dr. Fahrion concludes from this behaviour that the acids are split up through oxidation into other acids of low molecular weight. He experimentally shows that oleïc acid by the action of potassium permanganate produces acetic and oxalic acids, besides a mixture of other homologous acids, the presence of which also he could demonstrate when the oleïc acid was simply shaken with an alkali solution for three days. The acids from sardine oil showed analogous behaviour, but the volatile acids appeared in much larger quantities in both reactions.

Instead of ascertaining the iodine absorption of the oil-acids directly, Dr. Fahrion thought the results might be more correct if the solutions of the acids were first neutralised, because he had found that the polymerisation of the unsaturated acids was undone when they were saponified. In this way he obtained the following figures:—

| | Ordinary method | Neutral solution |
|---|---|---|
| Japanese oil . . . | 96·0 | 138·7 |
| Cod-liver oil . . . | 147·9 | 195·7 |
| Sardine oil . . . | 193·2 | 216·6 |
| Ricinoleïc acid . . | 82·9 | 102·9 |
| Oleïc acid . . . | 75·5 | 102·2–107·0 |
| Fluid acids from sardine oil . . . | 229·4 | 240·7 |

It will be seen that the figures for oleïc acid vary considerably when determined in a neutral solution, and are much higher than those theoretically correct (90·07), whereas the results as determined by the ordinary method are much too low. Dr. Fahrion therefore arrives at the conclusion that the methods hitherto in use are not reliable when hydroxy-acids are present, and proposes a method by which such acids are removed before the determination of iodine absorption. The method consists essentially in freeing the non-hydroxylated from the hydroxylated acids by the insolubility of the former in petroleum ether.

Dr. Fahrion (*Chem. Ztg.* 1893, xxx. 521).—Physetoleïc acid is generally supposed to be a characteristic constituent of fish oils, but so far as Dr. Fahrion has been able to determine it is found in sperm oil only, and not in any of the liver oils. If, however, it is a constituent of these, it must be in company with other unsaturated aliphatic acids, as is evident from the iodine absorption, which varies in different liver oils from 100 to 200, but mostly from 130 to 160, whereas the triglyceride of physetoleïc acid has an iodine absorption of 94·9 only. With a view to discovering physetoleïc acid in sardine oil, Dr. Fahrion examined it by the method described above, and found the fluid non-hydroxylic acids to consist chiefly of an acid isomeric to linolenic and isolinolenic acid of the formula $C_{18}H_{30}O_2$, of oily consistence and not solidifying in the cold. The different determinations gave the following figures, but he seems to admit that they more represent a selection made for the purpose than an average of all the results obtained.

| — | O | H | Iodine absorption | Acid-value | Saponif. value | Barium salt | Calcium salt | Magnesium salt |
|---|---|---|---|---|---|---|---|---|
| Found . . . . | 78·03 | 11·28 | 229·4 | 189·4 | 201·9 | 19·88 % | 6.63 | 4·25 |
| Calculated on $C_{18}H_{30}O_2$ . | 77·70 | 10·79 | 273·0 | 201·4 | 201·4 | 19·83 % | 6.73 | 4·15 |

This acid has consequently three double bonds, and Dr. Fahrion termed it *jecoric acid.*

Next he examined the solid acid of sardine oil, and found it to consist solely of palmitic acid, of which there was present as palmitin 14·3 per cent., determined by oxidising the unsaturated acids in the mixture by potassium permanganate.

According to the rule propounded by Hazura, jecoric acid ought to yield a hexahydroxy-stearic acid by oxidation with potassium permanganate. The fluid acids of sardine oil did not yield such an acid, but the result was a mixture of the lower homologues of the saturated aliphatic acid-series, among which carbonic acid was especially conspicuous. Dr. Fahrion explains this behaviour of jecoric acid by assuming that Hazura's rule holds good only as regards acids with a straight chain without branches, and that therefore jecoric acid must have a structure with side-chains, contrary to the opinion, hitherto entertained, that natural fatty acids never have side-chains.

Dr. Fahrion (*Chem. Ztg.* 1893, xxxix. 684) found palmitic acid in one variety of whale oil, as well as in sardine oil; and he then examined the solid acids in another whale oil, in Japanese oil, and in ordinary cod-liver oil. He prepared them by simply dissolving the acids in alcohol, exposing the solution to the cold, dissolving the crystalline mass thus obtained, and recrystallising it from alcohol until the colour was quite white. In this way he obtained from the oils mentioned solid acids with the respective melting points 54°, 61°, 56°, and 55°, and with the molecular weights 266·4, 260·6, 260·0, and 263·3. He concludes from these data that most fish and liver oils contain stearic in addition to palmitic acid, the latter, however, predominating. The so-called stearin from these oils is, he says, chiefly palmitin.

Dr. Fahrion has further made parallel determinations of Japanese oil, cod-liver oil, and sardine oil, with the following results:—

| — | Japanese oil | Cod-liver oil | Sardine oil |
|---|---|---|---|
| Specific gravity . . | 0·916 | 0·927 | 0·933 |
| Iodine-absorption . . | 96·0 | 147·9 | 193·2 |
| Acid-value . . . . | 31·2 | 15·8 | 20·6 |
| Ashes . . . . . | traces | traces | traces |
| Not saponifiable (cholesterin) . . . . | 0·6 | 0·6 | 0·6 |
| Total of fatty acids . | 95·3 | 94·9 | 94·5 |
| Hydroxy-acids . . | 0·5 | 0·6 | 0·7 |

The fluid acids were prepared from the barium salts through extraction by ether, and they were freed from hydroxy-acids, formed during the operations, by petroleum ether as described before. A yellow rather thin oil resulted, and the following determinations of the acids thus derived from the three different oils were made:—

| — | Acid-value | Iodine-absorption | Ultimate analysis | |
|---|---|---|---|---|
| | | | C | H |
| Japanese oil-acids . | 190·6 | 110·6 | 76·60 | 11·89 |
| Cod-liver oil-acids . | 184·0 | 175·5 | 78·02 | 11·53 |
| Sardine oil-acids . . | 189·4 | 229·4 | 78·03 | 11·28 |
| Calculated on $C_{18}H_{34}O_2$ | 198·6 | 89·9 | 76·59 | 12·06 |
| „ „ $C_{16}H_{30}O_2$ | 201·4 | 273·0 | 77·70 | 10·79 |

Except in the case of the sardine oil-acid, which according to Dr. Fahrion's earlier researches described above contains nearly exclusively jecoric acid, the ultimate analyses are rather purposeless, because evidently we have here to deal with mixtures of different acids. Dr. Fahrion says that jecoric acid is present in considerable quantities in cod-liver oil,[1] and that the larger percentage of hydrogen in these acids compared to those of sardine oil corresponds to the lower iodine-absorption. He further states that from the percentage of oxygen in the fluid acids the conclusion may be drawn, with considerable certainty, that the fresh oils contain no hydroxy-acids.

After having unsuccessfully tried to prepare the unsaturated acids, presumably present in cod-liver oil, by a method derived from the oxidation of fish oils in the process of chamois-dressing, Dr. Fahrion tried oxidation by potassium permanganate in alkaline solution. The acids thus hydroxylated from Japanese oil and insoluble in petroleum-ether were dissolved in a solution of sodium hydrate, precipitated by barium chloride, filtered at their boiling temperature, and to the filtrate was added hydrochloric acid in slight excess. When cooled, white mother-of-pearl-like crystals, m.p. 114° separated. The molecular weight of this was found by titration to be 302·4. The undissolved barium salt was decomposed by hydrochloric acid, again dissolved in sodium hydrate solution, and precipitated with barium chloride. This process was repeated five times, and still flakes of crystals separated when the filtrate was concentrated by evaporation. These flakes had m.p. 114°, and proved to be identical with the above-mentioned similar crystals. The small quantity of undissolved barium salt which remained was decomposed, and the acids recrystallised from alcohol. Their melting point was found to be 115°, and presumably identical with the rest. Cod-liver oil and sardine oil were treated in the same way; the product of oxidation from the former had m.p. 116°, mol. weight 304·9, and from sardine oil respectively 114° and 304·0. The yield from cod-liver oil was considerably smaller than that from Japanese oil, and from sardine oil still less. As there apparently could be no question of a mixture of different acids the determination by ultimate analysis was proceeded with, and the results were—

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[1] It does not appear from the papers Dr. Fahrion has published that he has actually and experimentally demonstrated the presence of jecoric acid in any other oil but sardine oil.

| — | C | H | Molecular weight |
|---|---|---|---|
| Found . . | 67·50<br>67·86 | 11·13<br>11·39 | 302·4 |
| Calculated for $C_{17}H_{34}O_4$ . | 67·55 | 11·26 | 302·0 |

This body, for which Dr. Fahrion proposes the name of *asellic acid*, is therefore the dihydroxy-heptadecylic acid from a heptadecylenic acid $C_{17}H_{32}O_2$ not yet isolated.

# NEW CHEMICAL RESEARCHES ON COD-LIVER OIL

By P. M. HEYERDAHL

## The Free Fatty Acids

In the determination of the amount of free fatty acids in cod-liver oil, Dr. Franz Hoffmann's method[1] was applied. Phenol-phthaleïne proved useless as an indicator in titration, and rosolic acid had to be used in its stead. The process was as follows:—

The oil, after being weighed—the amount varying from 7 grammes for oil containing small quantities of free fatty acids to 0·5 gramme for oil richer in these acids—was dissolved in 20–40 c.cm. of ether previously neutralised by $\frac{1}{100}$th of normal alcoholic solution of caustic potash, also used in titration of the fatty acids. It must be freshly prepared, as on standing a short time it alters in chemical composition. It is best made by taking the quantity necessary for immediate use of an aqueous $\frac{1}{10}$th normal solution of caustic potash, free from carbonic acid, and adding alcohol in the proportion of 1 to 10. If fat separates during titration more ether is added.

As indicator a couple of drops of an alcoholic solution of rosolic acid (4 : 1,000) is used.

During the titration exactly so much alcoholic solution of caustic potash is added to the liquid as will colour it a rose red. In the calculation of the acid-value the necessary correction must be made in case an acid ether or an acid alcohol has been used. By the acid-value is understood the number of milligrammes of KOH necessary to neutralise 1 gramme of fat.

With a view to determining the changes which the percentage of free acids of the oil underwent during the process of extraction from the livers, several samples taken from the oil at various stages of the process were examined by the above method. The free fatty acids, instead of increasing during the process, as one might have been inclined to expect, were actually found to decrease. Thus:—

| | At the beginning of the process | | At the end of the process |
|---|---|---|---|
| 1. Acid-value . | =0·76 | which decreased to | 0·58 |
| 2. „ . | =0·99 | „ „ | 0·81 |

By continued heating of the samples and simultaneously conducting a current of air through them, the acidity was at first somewhat decreased, but later it steadily rose, though not rapidly. For instance, the acid-value of a sample after being heated $1\frac{1}{2}$ hour on a water-bath, during which time a current of 52 litres of air was conducted through it, decreased from 0·81 to 0·75, but thereafter, during the next four hours, with an additional current of 155 litres of air, rose to 1·22. The other samples behaved in an analogous manner.

For oil extracted from the liver by freezing (no heat whatever being applied) the acid-value was found to be 1·38.

Oil prepared by conducting the steam direct into the liver had an acid-value of 0·27.

If a current of air was not conducted through the oil during the warming process the acid-value increased somewhat more slowly, though the difference was not great; for instance, after

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[1] *Beiträge zur Anatomie und Physiologie*, 1874.

165 minutes' heating, the acid-value rose from 0·68 to 0·75.

The influence of temperature upon the acid-value was exceedingly small. In a sample kept for over three hours, at a temperature of 243° C., the acid-value rose from 0·72 to 0·77 only.

Oil, rich in solid fats, had a smaller acid-value than oils from which they had been separated. The difference was 0·09.

In oil, melted from old (not fresh) fish-livers, a higher acid-value was found—in one case 1·75, for instance.

Oil melted from green (bilious) livers had an acid-value of 0·60.

In oil that had been standing a long time the free acids remained unchanged in quantity, *i.e.*

| | | | |
|---|---|---|---|
| Oil from 1884 | had an | acid-value of | 0·73 |
| „ 1885 | „ | „ | 0·74 |
| „ 1886 | „ | „ | 0·72 |
| „ 1887 | „ | „ | 0·70 |
| „ 1888 | „ | „ | 0·70 |

Several samples of raw medicinal oil were examined. Their qualities varied greatly, owing to want of uniformity in their preparation. The three samples indicated below varied in colour, odour, and taste :—

| | | | |
|---|---|---|---|
| The lightest sample | had an | acid value of | 7·38 |
| A somewhat darker | „ | „ | 7·55 |
| The darkest | „ | „ | 7·72 |

The acid-value of the pale oil was found to be 21·2, and of brown oil 54·4. These oils, which are separated from the liver by process of decay, thus show a very high acid percentage, which, of course, varies considerably, according to the quality of the oil.

For oil obtained from other species of fish by the steam process the following acid-values were found :—

| | | | |
|---|---|---|---|
| Coal-fish (*Gadus virens*) oil | had an | acid-value of | 0·34 |
| Torsk (*Brosmius brosme*) | „ | „ | 0·15 |
| Ling (*Molva vulgaris*) | „ | „ | 8·51 |
| Starry Ray (*Raia radiata*) | „ | „ | 9·34 |
| Porbeagle (*Lamna cornubica*) | „ | „ | 5·10 |

As will be seen, the free fatty acids of oil prepared from cod-livers by steam process are insignificant, the acid-value of 0·70 corresponding to 0·36 per cent. of oleic acid. The acid percentage is increased very little indeed by heating even to quite high temperatures, while, on the other hand, its colour darkens, and its rancidity increases with great rapidity. The free fatty acids have consequently no connection with rancidity; they are, however, greatly inclined to form during the decay of the liver, but neither during the application of heat nor through the influence of the air.

### Examination of Stearin

The Trade demands that the finest medicinal cod-liver oil shall remain perfectly clear, and deposit no solid fats at low temperatures, some placing the limit at 0° C., and others still lower.

The solid fats, which under the influence of cold are deposited by the oil, go under the common name of *stearin*, a white butter-like mass, which has hitherto been supposed to consist mainly of palmitin, stearin, and some oleïn, and the melting-point to vary according to the proportion in which these three glycerides were present.

It would naturally be of interest to submit this so-called stearin to a closer examination, and to this end attempts were made to prepare the solid, free from the fluid glycerides, by repeated crystallisations in ether, ether-alcohol, and petroleum-ether. v. Hübl's iodine-absorption method was applied for determining the degree of purity of the crystallised substance. Stearic and palmitic acids are, as is well known, saturated compounds, which add no iodine from v. Hübl's solution, so that the more these were freed from oleïc acid the less should be the iodine-absorption, until at last, when all oleïc acid, in the form of oleïn, was washed away, the iodine-absorption should be 0. As a means of control, determinations of acid-value and melting-point were applied. The determination of iodine-absorption, according to v. Hübl's method, was as follows :—

The amount of oil used for each determination varied from 0·2 to 0·4 gramme. In order always to have nearly equal weight, the same number of drops of the oil were taken and these accurately weighed, dissolved in chloroform in a 200 c.cm. bottle having a glass stopper. Chloroform was added in such quantity that the liquid remained clear during titration, as a rule 18 c.cm. being sufficient. The iodine solution was made by mixing 25 grammes of iodine, dissolved in 500 c.cm. of alcohol, with 30 grammes of chloride of mercury, also dissolved in 500 c.cm. of alcohol, and allowing the mixture to stand twenty-four hours. This solution was then added from a burette in such quantity that after standing two hours the dark brown colour still remained; 25 c.cm. proved a proper amount.

The mixture was set aside for a certain time, which for all samples must be the same in order to obtain comparable results—in this case two hours—at the expiration of which was added such quantity of a 10-per-cent. iodide of potassium solution that upon the admixture of 150 c.cm. of water no iodide of mercury was deposited: 20 c.cm. of iodide of potassium solution proved sufficient.

Lastly, the liquid was titrated with sodium thiosulphate solution during constant stirring until it assumed a light yellow colour, when a few drops of a fresh starch solution were added as an indicator; the titration with sodium thiosulphate was then resumed, and continued until all colour disappeared. The shades of the liquid from the time of the addition of the starch solution until decoloration varied from a mossy green, through green, and bluish green to violet, from which point, a couple of drops only, of the sodium thiosulphate solution, were required to complete the process.

In this manner were examined by way of a beginning:—

1. Steam-prepared oil from which the solid fats had been removed at −7°.

2. Steam-prepared oil from which no solid fats had been removed.

3. The solid fats (so-called stearin), freed as much as possible by mechanical means from the liquid fats.

For No. 1 the iodine-absorption was found to be =142·6
For No. 2 " " " =140·1
For No. 3 " , " =113·4

The inconsiderable difference between the first two figures shows that the iodine-absorption method is little adapted to determining the percentage of solid glycerides in the oil, and the last figure proves that the so-called stearin contains considerable quantities of iodine-absorbing matter.

As before stated, the stearin had been experimentally recrystallised from ether, ether-alcohol, and petroleum-ether. It seemed to crystallise best from the last-named solvent, but it retained an iodine-absorption of 97·7 after repeated crystallisation from this medium, and must therefore be supposed to contain still a considerable quantity of unsaturated compounds. As it would obviously be a rather impracticable way to obtain the solid fats by recrystallisation, the method was abandoned, and replaced by a process of isolating the solid acids, in order to obtain through them some knowledge of the solid compounds in the stearin.

To this end 200 grammes of stearin were saponified with a 20-per-cent. *aqueous* solution of caustic soda in excess, added in small quantities during constant stirring and heating over a water-bath, and, later, over open fire 8½ hours. There remained an unsaponifiable residue. The under lye was now drawn off, the rest warmed with 1,200 c.cm. of water, cooled, and set aside in a deep beaker glass.

The unsaponifiable part, which separated as a white, butter-like floating mass, was removed and repeatedly washed with warm water, from which it was freed in a separating funnel. The substance now separated into two layers, the upper one yellow and butter-like, the lower rather whiter. Separated from each other and thoroughly washed with water whilst being heated over a water-bath, their iodine-absorption was found to be—

1. The yellow butter-like substance =119·1
2. The whiter substance =116·2

or, both more iodine-absorbing than 'stearin.'

Both were saponifiable with *alcoholic* solution of sodium hydrate. The soap was heated over a water-bath until the alcohol had evaporated, and then decomposed with dilute sulphuric acid. The free acids thus obtained were repeatedly washed with water until the washing water gave no deposit with $BaCl_2$, and then subjected to the iodine-absorption test—

For acid obtained from the substance 1 it was found to be . . . . . . . . = 119·8
For acid obtained from the substance 2 it was found to be . . . . . . . . = 114·6

After the aqueous soap-solution had been freed from the substances unsaponifiable in aqueous solution of caustic soda, dilute sulphuric acid was added until an acid reaction was obtained, when the fatty acids separated upon the surface as a white layer; this was skimmed off and repeatedly washed with warm water until the water no longer gave a deposit with $BaCl_2$. A brown flocky substance deposited in the mixture of acids and was filtered off in a hot-water funnel; it was soluble in caustic soda solution. The iodine-absorption of the mixture of acids was found to be = 103·7.

For the purpose of isolating the solid acids of the mixture, it was subjected to fractional distillation under diminished pressure. A thermometer was inserted in the distilling flask, and a capillary tube led to the bottom in order that a current of dry carbonic acid might be introduced with a view to preventing percussive ebullition. With the same end in view, several loose capillary tubes were placed in the flask, and the whole heated on a graphite bath. The distilling flask was in air-tight connection with a receiver, which again was connected with a suction pump and a mercurial manometer.

During the first part of the distillation the temperature rose uninterruptedly to 280° (80 mm. pressure). That which passed over during this time was essentially water with a little acid that spurted over.

Between the temperatures 280° and 305° a white, slightly yellowish, acid of crystalline appearance distilled over (distillate 1).

That which passed over at temperatures above 305° was of a somewhat more yellow colour (distillate 2).

The residue in the distilling flask had now become rather thick and of a dark brown colour.

The melting-point, which in the case of the acid mixture before the distillation was found to be 32°, was now found to be

Of the distillate 1 = 36°
" 2 = 31°

The iodine-absorption was found to be

Of distillate 1 . . = 59·1
" 2 . . = 69·1
Of the residue in the flask . = 95·1

Upon redistillation, the melting-point of distillate 1 rose to 38°, while the iodine-absorption was somewhat lowered. The acid value was found to be 270, while that of the mixture before distillation was 236.

After recrystallisation from alcohol the iodine-absorption fell to 22·4, and the melting-point rose to 55°; the acid value was now 203.

If, then, we suppose that the 'stearin' is a mixture of glycerides of saturated and unsaturated acids, the former having an iodine-absorption of 142·6, the percentage of the latter in cod-liver oil might be calculated when it is remembered that the 'stearin,' the iodine-absorption of which was found to be 113·4, constitutes about 10 per cent. of cod-liver oil.

The percentage of glycerides of unsaturated acids in the 'stearin' = $\frac{100,113\cdot4}{142\cdot6}$, about 80 per cent.

The percentage of glycerides of saturated acids in the 'stearin' will, therefore, amount to 20 per cent., and as, at most, $\frac{1}{10}$th of the oil is 'stearin,' the amount of glycerides of the saturated acids (palmitic and stearic acids) from which cod-liver oil is supposed to be freed by the freezing process, at 7° of cold, can at the outside be only 2 per cent., probably much less, as will be explained hereafter.

### THE EXISTENCE OF HYDROXY-ACIDS IN COD-LIVER OIL.

Benedikt and Ulzer[1] have devised a method for determining the percentage of hydroxy-acids contained in fats by acetylating their fatty acids. Those of the acids which contain no hydroxyl-group are not affected by the acetylation; the difference between the amount of potassium hydrate necessary for saponification and that required for neutralising the acetylated fatty acids will be in direct proportion to the amount of hydroxy-acids which they contain. If a non-acetylated fatty acid contains $x$ hydroxyls the quantity of potassium hydrate necessary for saponification after acetylation will be $x$ times as large as the quantity required for neutralisation. True, in case the nature of the fatty acid in question be unknown, it will be impossible to determine the percentage of hydroxy-acids, but valuable points may be gained for isolating and identifying the fats.

The process in its details is as follows:—

One hundred grammes of oil are boiled in a flask with inverted condenser, together with 70 grammes of potassium hydrate dissolved in 50 c.cm. of water and 150 c.cm. of strong spirit until thoroughly saponified, whereupon the whole contents of the flask are poured into a large porcelain basin, a litre of water is added, and sufficient dilute sulphuric acid until acid reaction. The mixture is then boiled until the fatty acids rise to the surface in the form of a perfectly clear layer, and the alcohol is evaporated.

The fatty acid layer is now boiled twice with water, separated, dried in hot-air bath at 30°, and filtered through a dry filter.

Fifty grammes of the fatty acids thus obtained are now boiled with 40 grammes of acetic anhydride for two hours in a flask with inverted condenser, and then poured into a deep beaker-glass; 500 c.cm. of hot water are added, and the whole boiled. In order to prevent percussive ebullition a weak current of carbonic acid is conducted through a capillary tube to the bottom of the glass. After boiling for some time the water is poured off, and the acetylated fatty acids, being again boiled three times with 500 c.cm. of water, now no longer colour litmus paper red, a sign that all acetic acid has evaporated. The acetylated fatty acids separated from the water are dried in a hot-air bath at 30°, and filtered through a dry filter.

For the determination of their acid-value 4 to 5 grammes of the acetylated acids thus obtained are dissolved in spirit, which must be free from fusel oil and acid, and, after the addition of phenol-phthaleïne as indicator, titrated with half normal solution of potassium hydrate.

About 1·5 gramme of the acids were used for the determination of the saponification-value. Besides the half-normal solutions of potassium hydrate and hydrochloric acid an alcoholic solution of caustic potash is now required. This is prepared by dissolving about 30 grammes of potassium hydrate, previously washed with alcohol in as little water as possible, diluting with alcohol, free from fusel oil, to one litre. The solution is set aside for two days and filtered. As the solution undergoes changes on standing, only a quantity sufficient for immediate use is prepared.

The acetylated acids are now weighed out in a flask of 100 c.cm. capacity, and exactly 25 c.cm. of the alcoholic solution of caustic potash are added from a pipette. The mouth of the flask is covered with a funnel, and the contents subjected to gentle boiling on a water-bath for fifteen minutes, phenol-phthaleïne added, and the excess of alkali retitrated with hydrochloric acid. The strength of the caustic potash solution is determined in a similar way by heating 25 c.cm. of it over a water-bath for fifteen minutes, adding phenol-phthaleïne, and titrating with hydrochloric acid. Taking the difference between this titration and the first, the amount of potassium hydrate used in saponification may be easily calculated, and from this result the saponification value determined.

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[1] *Zeitschr. f. ch. Industrie*, 1887, p. 149.

By this method the percentage of hydroxy-acids in cod-liver oil was examined, but they proved to possess qualities differing from those of other fatty acids examined by Benedikt and Ulzer, and which had to be taken into account in the determination of the acid- and saponification-value.

Thus, in the determination of acid-value it was not sufficient to simply dissolve the acetylated acids in alcohol, as stated before, and then titrate with KOH, because not only did it displace the hydrogen in the carboxyl-group, but split off some of the acetyls at the same time. To prevent the latter, it became necessary to dilute the solution so much that the solution of potassium hydrate became too weak to affect the acetyls. By dissolving the acetylated acids in 150 c.cm. of alcohol, agreeing results were obtained, and the reaction set in instantly without splitting off any acetyls.

In the determination of the saponification-value a difficulty was encountered by the solution of the acetylated acids assuming such a dark brown colour as to totally obscure that of phenol-phthaleïne; therefore, the change from alkaline to acid reaction could not be observed. Other indicators which were tried, such as rosolic acid, alkanet, galleïn, phenacetolin, and congo-paper, proved equally worthless. By diluting with ½ litre of water it became possible to distinguish the colour changes and obtain serviceable results.

Still, even after these improvements in the process had been made, the percentage of hydroxy-acids was found to be very irregular. Some of the results are stated here :—

| Acetylated acids from | Acid-value | Saponification-value | Acetyl-value |
|---|---|---|---|
| 1. Cod-liver oil free from stearin . | 169·1<br>169·4 } 169·3 | 203·2<br>207·9 } 202·8<br>197·2 | 33·5 |
| 2. Cod-liver oil free from stearin . | 170·8 | 207·7 | 36·9 |
| 3. Cod-liver oil containing stearin . | 176·3<br>175·2 } 175·8 | 200·1<br>201·7 } 200·9 | 25·1 |
| 4. Stearin . . | 174·4<br>174·4 } 174·4 | 177·7<br>175·5 } 176·6 | 2·2 |

From these figures it will be seen that very different acetyl-values have been found for two acetylated acids produced from the same oil, and even that the acid-values of the same acetylated acid do not agree. This irregularity is still more striking in the saponification-values which show, for acids prepared from the same oil a variation of from 197·2 to 207·9—a difference of 10·7.

On account of these irregularities, notwithstanding the greatest care taken in all the operations and in spite of the high iodine-absorption which would seem to point to a scarcity of hydroxy-acids, the presence of a disturbing element was apparent, and the agency of the air was suspected.

This supposition was confirmed in the most satisfactory manner by excluding the air and replacing it by hydrogen. Numerous experiments proved the necessity of this replacement of air by hydrogen, or some other inert gas, not only during the saponification of the oil and the preparation of the free fatty acids, but also during the whole of the analytical operations, acetylation, washing, filtering, and even during the determination of acid- and saponification-value.

The results now obtained varied considerably from those given above, and were of eminent interest :—

| Acetylated acids from | Acid-value | Saponification-value | Acetyl-value |
|---|---|---|---|
| 1. Cod-liver oil free from stearin . | 191·7 | 193·8 | 2·1 |
| 2. Cod-liver oil free from stearin . | 191·8<br>191·9 } 191·8 | 193·9<br>193·7 } 193·8 | 2·0 |
| 3. Stearin . . | 196·3<br>196·2 } 196·3 | 197·2<br>197·3 } 197·3 | 1·0 |

By way of comparison the acids of linseed oil were acetylated in air and in hydrogen, but it was found that air did not affect the acids in regard to their percentage of hydroxy-acids. This was rather unexpected—on account of their high iodine-absorption.

Thus it is a unique peculiarity of cod-liver oil that it oxidises with such extreme ease upon being heated in air, and this property of giving greatly differing acetyl-values upon parallel acetylation in hydrogen and air, may be used as a specific test for cod-liver oil.

As the oil proved so exceedingly sensitive when heated in air, it must be supposed as a matter of course, that it oxidised in the process of preparation, during which the air had free access both whilst the livers were being heated by steam and afterwards, and that its percentage of hydroxy-acids, corresponding to the acetyl-value 2·0 as demonstrated above, was due to this cause. If an inert gas replaced the air during the process of preparation the oil would in all probability be free from hydroxy-acids, and the acetyl-value would be found to be = 0.

This supposition was fully confirmed by practical experiment.

For cod-liver oil prepared in a current of carbonic acid the following results were obtained:—

| | Acid-value | Saponification-value | Acetyl-value |
|---|---|---|---|
| 1. | 191·5 | 191·5 | 0·0 |
| 2. | 194·6 | 194·7 | 0·1 |

The analysis was, of course, carried out under the precautions enumerated above. It is probably due to a difference in the percentage of stearin that the acid and saponification values in one case are a trifle lower than those in the other.

During the acetylating experiment it was again observed, as before during the determination of free fatty acids, that the oil assumed a darker colour, and acquired a rancid taste and odour. On the other hand, when heated in inert gases it remained almost unchanged. *The rancidity of the oil is therefore caused by the formation of hydroxy-acids, and not by its splitting up into free acids.*

Of course, the iodine-absorption must be in inverse ratio to the proportion of hydroxy-acids in the oil; and as this determination is much easier and quicker than that of acetyl-value, it might with advantage be applied in cases where the same percentage of stearin in different oils to be examined has been insured.

Some of the analyses carried out with this point in view are here placed together for comparison:—

| — | Acetylated: protected from oxidation | Acetylated: not protected from oxidation |
|---|---|---|
| *From the Oil* | | |
| Acid-value | 191·8 | 169·3 |
| Saponification-value | 193·8 | 207·8 |
| Acetyl-value | 2·0 | 38·5 |
| Iodine-absorption | 157·7 | 105·6 |
| *From the Stearin* | | |
| Acid-value | 196·3 | 174·4 |
| Saponification-value | 197·3 | 176·6 |
| Acetyl-value | 1·0 | 2·2 |
| Iodine-absorption | 116·7 | 103·2 |

From these figures it will be seen what an extraordinary influence the percentage of hydroxy-acids has upon the iodine-absorption; while the difference between the acetyl-values of the oxidised and non-oxidised oils is 36·5, the difference in iodine-absorption is 52·1. Thus, given the percentage of stearin, the percentage of hydroxy-acids (*i.e.* the degree of rancidity) of the oil may be pretty accurately determined by the iodine-absorption.

As the percentages of both stearin and hydroxy-acids tend to diminish the iodine-absorption, the chemical expression for the best oil in the estimation of *the trade* must be the highest possible iodine-absorption.

It will now be understood that the 2 per cent. of saturated acids found by the examination of stearin, or the greater part at least, were hydroxy-acids formed from unsaturated acids by the action of the air during the progress of analysis.

## BROMINE ABSORPTION

To 200 grammes of cod-liver oil, from which the solid fats ('stearin') had been separated by cooling in a freezing-mixture and filtering through cotton-cloth, were added 140 grammes of potassium hydrate dissolved in 100 c.cm. of water and 300 c.cm. of alcohol. The whole was heated in a current of hydrogen until thoroughly saponified, then diluted with 1½ litre of warm water, and dilute sulphuric acid added until an acid reaction was obtained. The mixture was boiled until the fatty acids separated in the form of a clear floating layer, the water poured off, and the fatty acids further washed three times in boiling water, all the time in a current of hydrogen. The water poured off the acids was filtered: in this way 178 grammes of fatty acids were obtained, part of which, solid at ordinary temperatures, was isolated in a suction-filter.

One hundred grammes of the fluid acids were dissolved in 300 c.cm. of pure glacial acetic acid, cooled in a freezing-mixture, and 38 c.cm. of bromine added, drop by drop, during constant stirring. The solid bromine-compounds thus produced were separated from the liquid and dried on tiles. After being washed with spirits, 20 grammes of these bromine products were repeatedly boiled with alcohol of 96 per cent.; the liquid was drawn off and the insoluble part dried, first between filtering-paper and then in vacuo over concentrated sulphuric acid. In this manner a white solid substance was obtained, which was almost insoluble in alcohol, ether, chloroform, benzene, and glacial acetic acid. After renewed repeated boiling in alcohol its percentage of bromine, when determined by igniting it with pure quicklime, was found to be constant.

Two bromine-determinations gave:

1. 70·80 per cent. bromine
2. 71·01 „ „

The ultimate analysis of the bromine product gave:

| | C | H |
|---|---|---|
| 1. | 22·40 per cent. | 3·00 per cent. |
| 2. | 22·50 „ | 2·99 „ |

Calculated from the formula $C_{17}H_{26}Br_8O_2$:

22·59 per cent. C, 2·88 per cent. H, and 70·95 per cent. Br.

This corresponds to the figures obtained.

The bromine in the compound $C_{17}H_{26}Br_8O_2$ may have entered either by addition, or by substitution, or by both. If the bromine entered into the compound, entirely or partly, by substitution, a molecule HBr would be formed for every hydrogen-atom substituted in the acid by bromine. We can, therefore, ascertain how much bromine is present by substitution in the compound $C_{17}H_{26}Br_8O_2$ when we determine the quantity of HBr formed during the process of bromation.

For this purpose 10 grammes of the fluid acids were dissolved in chloroform, and to the solution, cooled in a freezing-mixture, 3·6 c.cm. of bromine were added, drop by drop, during continual stirring. The bromine compound was separated by filtration and the filtrate agitated with 600 c.cm. water, separating the rest of bromine-compound which was filtered off. The chloroform being separated from the water was again agitated with 100 c.cm. of water and the two watery extracts united, filtered, and precipitated by silver-nitrate; 0·04 grm. of silver bromide was thus obtained corresponding to 0·02 grm. hydrobromic acid. Suppose, now, that one, only, atom of hydrogen had been substituted by bromine in $C_{17}H_{26}Br_8O_2$, then no less than 3 grammes HBr would have been formed from the 10 grammes of the original acid instead of the 0·02 gramme actually found. *Consequently all bromine atoms must have entered the compound* $C_{17}H_{26}Br_8O_2$ *by addition*, and the original acid must have been an unsaturated fatty acid of the formula $C_{17}H_{26}O_2$.

From experiments made so far, this remarkable acid seems to be present to the extent of about 20 per cent.; on account of its peculiar properties and structure, coupled with the large percentage in which it is present, it probably plays an important, perhaps the most important, part in the therapeutical action of cod-liver oil and therefore I propose to give it the name of '*therapic acid.*' Its saturated bromine combination would then be octo-bromo-therapic acid, or octo-bromo-margaric acid, if we look upon it as a saturated acid.

## THE OXIDATION OF THE FATTY ACIDS OF COD-LIVER OIL BY POTASSIUM PERMANGANATE

K. Hazura has propounded the following rule for unsaturated acids: 'Unsaturated fatty acids in alkaline solution add, when oxidised by potassium permanganate, as many hydroxyl-groups as there are free valencies in the acids, and form saturated hydroxy-acids, with the same number of carbon-atoms in the molecule.' The acids of the oil or fat are isolated and oxidised in alkaline solution by potassium permanganate, the composition of the hydroxy-acids produced is determined, and from their percentage of carbon and number of hydroxyl groups a conclusion is drawn of the carbon percentage, and number of free valencies in the original unsaturated acids.

The fluid fatty acids of cod-liver oil were oxidised according to this method; 30 grammes of these acids, prepared from oil free from stearin and separated from the solid acids in a suction-filter, at ordinary temperature, were saponified by 36 c.cm. of caustic potash solution, specific gravity 1·27. The soap was dissolved in 2 litres of water, and 2 litres of a $1\frac{1}{2}$-per-cent. solution of potassium permanganate were slowly added during constant stirring. After being set aside for ten minutes the oxidation was cut short by reduction with an aqueous solution of sulphurous acid, which was added until all unchanged potassium permanganate was reduced to hydrated manganese peroxide, and this again dissolved. About 2 grammes of a white solid substance, insoluble in cold water, were formed and filtered off through cotton-cloth. This yield being so insignificant the natural conclusion was that the bulk of hydroxy-acids would be found in the aqueous solution; the solution was then filtered anew in order to free it from every trace of insoluble acids, and KOH added until a slight alkaline reaction was obtained. The liquid was then evaporated to a volume of 300 c.cm. and, after being cooled, sulphuric acid was added, to acid reaction.

The precipitated manganese peroxide was exactly reduced by sulphurous acid, after which the liquid was distilled in a current of steam in order to get rid of volatile acids, possibly present. The residue ought now to contain the non-volatile hydroxy-acids soluble in water. The brown-coloured liquid was concentrated by evaporation, cooled, and agitated with ether, which, however, did not extract anything. $Na_2CO_3$ was then added until alkaline reaction, the liquid boiled, and the manganese precipitate produced was removed by filtration; the filtrate, evaporated to dryness on a water-bath, was extracted with alcohol of 80 per cent. by boiling in a flask with inverted condenser. In this way a brown syrupy fluid was obtained, but no hydroxy-acids.

The result of these investigations was, then, that only a couple of grammes of solid, in water insoluble, hydroxy-acids were obtainable from 50 grammes of original acids. The natural inference was, therefore, that the oxidation had struck deeper than intended, and that the method as described above was useless for the preparation of hydroxy-acids from the acids of cod-liver oil.

After several unsuccessful attempts to gain the desired end, it was at last found that the oxidation had to be proceeded with at a temperature of 0°, and by a stronger solution of potassium permanganate. Half-saturated solution of $KMnO_4$ gave good results. Thus, the acid which yields the hydroxy-acid described below has the property of being very sensitive to oxidation at ordinary temperatures, but can at a low temperature bear a powerful oxidation without being split up.

The white, in cold water insoluble, oxidation product was filtered off through cotton-cloth, repeatedly washed with cold water, dried on tiles, and then extracted with cold ether. After the ether had been distilled off, the mixture of hydroxy-acids (m.p. 110°) was treated with boiling water, in which it was partly soluble. But as the soluble part had its m.p. at 180°, and the insoluble at nearly 200°, and as besides, both turned brown on being heated to the melting point—which was not the case with the original mixture—it was apparent that the two bodies were decomposition products. It was to be apprehended that heating with aqueous ether or alcohol might also split up the hydroxy-acids; they were, therefore, now recrystallised from chloroform after being dried on tiles. After many recrystallisations a product was obtained with melting point between 114° and 116°.

The ultimate analysis of this hydroxy-acid gave the following result:—

| | Found | Calculated for $C_{19}H_{38}O_4$ |
|---|---|---|
| C . . | 68·77 | 69·09 |
| H . . | 11·34 | 11·50 |

The molecular weight was determined from the acid value. About 2·5 grammes hydroxy-acid were dissolved in 100 c.cm. of alcohol (free from acid) and titrated with $\frac{1}{2}$n. solution of potassium hydrate in excess. The excess was retitrated with $\frac{1}{20}$n. HCl.

| | | Calculated for $C_{19}H_{38}O_4$ |
|---|---|---|
| 1. 2·3397 grms. ⎰ hydroxy-acid | 170·8 | 169·7 |
| 2. 2·7598 grms. ⎱ gave acid-value | 171·3 | |

The molecular weight calculated from these figures.

| | | Calculated for $C_{19}H_{38}O_4$ |
|---|---|---|
| 1. . . | 327·8 | 330·0 |
| 2. . . | 326·9 | |

The percentage of hydroxyls in the hydroxy-acid was determined by the acetylation method; 8 grms. of acid were boiled for two hours with 40 grms. acetic anhydride in a flask with inverted condenser. The acetyl acid thus produced was freed from acetic acid by boiling four times with $\frac{1}{2}$ litre water. After separating it from water, acid-value and saponification-value were determined.

4·541 grms. acetylated acid were dissolved in 150 c.cm. acid-free alcohol and titrated with $\frac{1}{2}$n. solution of potassium hydrate.

| | | Calculated for $C_{19}H_{36}O_4\,(C_2H_3O)_2$ |
|---|---|---|
| Acid-value was found to be | 134·8 | 135·2 |

1·327 grms acetylated acid were saponified on a water-bath with alcoholic solution of caustic potash for fifteen minutes. The excess was retitrated with $\frac{1}{2}$n. HCl.

| | | Calculated for $C_{19}H_{36}O_4(C_2H_3O)_2$ |
|---|---|---|
| Saponification-value was found | = 411·9 | 405·8 |

The number of hydroxyl groups is calculated from the acid-value and saponification-value:—

$$134{\cdot}8 : 411{\cdot}9 = 1 : 3{\cdot}05$$

It will be seen from this equation that the hydroxy-acid contains two hydroxyl groups, and therefore has the formula $C_{19}H_{36}O_2(OH)_2$.

From the acid-value of the acetylated acid, 134·8, the molecular weight may be calculated.

| | Found | Calculated for $C_{19}H_{36}O_4(C_2H_3O)_2$ |
|---|---|---|
| Molecular weight . | 415·5 | 414·0 |

The silver salt of the hydroxy-acid was prepared in the following manner:—

The hydroxy-acid was heated upon a water-bath with ammonia until it was thoroughly saponified and the excess of the latter evaporated. Silver nitrate was added in excess to the hot soap solution. The precipitate was first washed with cold and then with warm water until the water no longer gave reaction on silver. The precipitate was heated with ether, in a flask with inverted condenser, upon a water-bath several times until the separated ether on evaporation left no residue. After drying to constant weight, its percentage of silver was determined:—

| | Calculated for $C_{19}H_{37}AgO_4$ |
|---|---|
| 1. 0·4120 grm. silver salt gave<br>0·1021 grm. Ag = 24·78 per cent. | 24·66 |
| 2. 0·4154 grm. silver salt gave<br>0·1027 grm. Ag = 24·72 per cent. | |

All the results obtained as above agree well with the corresponding figures for the hydroxy-acid, $C_{19}H_{38}O_4$. This formula for the hydroxy-acid under consideration is therefore scarcely questionable, and it is beyond doubt that it was prepared by oxidation from a corresponding unsaturated acid of the fluid acids of the oil, by two hydroxyls entering its double bond. I propose for this unsaturated acid the name of *jecoleïc acid*, derived from its origin; the corresponding hydroxy-acid would then have to be designated as di-hydroxy-jecoleïc acid.[1]

As demonstrated above, the yield of hydroxy-acids is exceedingly small so long as the oxidation is performed at temperatures above 0°; it is therefore probable that the acids are split up at higher temperatures; even the hydroxy-acids break up on boiling with water. This peculiar property of the acids appears to be closely connected with the therapeutical properties of cod-liver oil.

## The Saturated Acids of Cod-liver Oil

By the saponification of cod-liver oil, from which the fats that are solid at low temperatures had been removed, and by the following decomposition of the soap, a mixture of acids was obtained, from which, as already mentioned, a substance solid at ordinary temperatures separated. After repeated recrystallisations from alcohol a white solid acid crystallised in glancing plates, with constant m.p. 62°.

The acid-value was determined:—

| | | Calculated for $C_{16}H_{32}O_2$ |
|---|---|---|
| 1. 2·4638 grms. acid gave acid-value | =217·2 | 218·8 |
| 2. 2·1189 grms. „ „ | =217·1 | |

The molecular weight calculated from these figures:—

| | | |
|---|---|---|
| 1. . . | 257·8 | 256·0 |
| 2. . . | 257·9 | |

The silver salt was prepared in exactly the same manner as that of hydroxy-jecoleïc acid (p. xcvii). The percentage of silver was found to be:—

| | Calculated for $C_{16}H_{31}AgO_2$ |
|---|---|
| 1. 0·3599 grm. silver salt gave 0·1063 grm. Ag =29·53 per cent. | 29·69 |
| 2. 0·3366 grm. silver salt gave 0·0998 grm. Ag =29·65 per cent. | |

v. Hübl's iodine-absorption method was applied, for ascertaining whether it were a saturated acid or not.

0·3966 grm. acid was dissolved in 18 c.cm. of chloroform and 25 c.cm. of v. Hübl's iodine solution were added. After a lapse of two hours the fluid was titrated with sodium-thiosulphate in the ordinary way; 43·43 c.cm. were required. 25 c.cm. of iodine solution + 18 c.cm. of chloroform required likewise 43·43 c.cm. of sodium thiosulphate; consequently the iodine absorption was = 0, and the acid was therefore a saturated fatty acid, and evidently *palmitic acid.*

## Percentage of the Acids found in Cod-liver Oil

It cannot yet be conclusively stated in what proportions the acids discussed above are present in the oil. There are probably more, hitherto unknown, acids which have not as yet been determined, and these researches were not made with a view to quantitative determination. However, some conclusions may be drawn from them and from iodine-absorption determinations.

The mixture of acids prepared from oil free from stearin contains—

| | |
|---|---|
| 4 per cent. | palmitic acid, or less |
| 20 „ | therapic acid, |
| and, 20 „ | jecoleïc acid, at least. |

The remaining moiety consists, in all likelihood, of one or more lower unsaturated acids with one double bond, or perhaps a mixture of such an acid and jecoleïc acid.

The author hopes at some not very distant day to be enabled to give further particulars on this subject and of continued researches on the acids discussed above and on cod-liver oil generally.

## Researches on Ptomaïnes in Cod-liver Oil

Raw medicinal oil was examined according to the method of A. Gautier and L. Mourgues.[1] The oil which was employed for this purpose was that which rises, first of all, to the surface from the livers set aside for putrefaction; consequently, raw medicinal cod-liver oil of the lightest colour met with in trade.

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[1] How far jecoleïc acid is identical to doeglic acid, which has the same percentage composition, cannot yet be decided. They are probably isomers.

[1] *Les alcaloïdes de l'huile de foie de morue.*

One hundred kilos. of this oil were agitated with the same volume of spirits of 33 per cent., in which 4 grammes of oxalic acid were dissolved in every litre. The emulsion produced was set aside and the spirit when separated poured off. Milk of lime was added to the spirit until only a slightly acid reaction remained. The greater part of the oxalic acid and some inevitably accompanying fat-particles were precipitated as oxalic and aliphatic calcium salts, and were removed by filtration. The liquid was then distilled under diminished pressure upon a water-bath at temperatures varying from 35° to 55°, with some capillary tubes in the distilling flask to prevent percussive ebullition. In this way the liquid was evaporated to $\frac{1}{20}$th of its original volume. The concentrated liquid was digested with freshly-precipitated calcium carbonate until neutralisation. The precipitated calcium oxalate was removed by filtration, and a few drops of lime-water, until alkaline reaction, added to the filtrate, which was then distilled to dryness at 50°, under diminished pressure. The residue was dissolved in spirit (90 per cent.), filtered and redistilled under diminished pressure; mixed with a small quantity of water, solid potassium hydrate added, and the whole agitated with ether. To the ethereal solution oxalic acid was added, and to the exceedingly insignificant precipitate, two or three drops of water and some potassium hydrate were again added, when a few milligrammes of an intensely strong smelling oil separated on the surface. The quantity was too small for any closer examination.

This result proves that ptomaïnes have not had time to form, and in the raw oil, therefore, are present only to an extremely trifling and insignificant extent.

This agrees with the results of Gautier's and Mourgues' experiments.

## CONCLUDING REMARKS

It is generally admitted that the therapeutical action of cod-liver oil is one entirely its own; the peculiar benefits derived from its employment in nervous, rheumatic, scrofulous, phthisical, and other diseases are not to be obtained from any other remedy whatsoever. It is therefore by no means wonderful that the scientific mind has been occupied ever since the early days of organic analysis in attempts at discovering the exact nature of the constituents which give cod-liver oil its special value. A synopsis of the more important of these researches is given in the preceding pages by Mr. Heyerdahl, together with a full account of his own investigations. These are drawn up in the style that is supposed to be orthodox for scientific communications, the bare facts being recorded, and the reader left to digest them as best he can. The writer may therefore be permitted to add this supplement in which the facts will be presented in a somewhat more predigested form, and some of their theoretical and practical consequences will be pointed out.

The first chemical research on cod-liver oil was by Wurzer, and dates as far back as 1822. This investigator seems to have come across the the *ptomaïnes* which Gautier and Mourgues discovered sixty-six years later, but he had not our present means of determining them. Spaarman (1828) found that the oil contained 97 per cent. of the glycerides of *margaric, oleïc*, and *delphinic*—now called valerianic—*acids*, besides 3 per cent. of *colouring* and *odorous substances*. Marder (1830) discovered that the oil contained *chlorides* and *sulphates*; *iodine* was discovered by Hopfer de l'Orme (1836); to this *bromine* was added by Herberger and *phosphorus* by de Vrij (1838). A most elaborate qualitative and quantitative analysis was made by de Jongh in the year 1843. He found that the oil contained *gaduin*, certain *biliary constituents*, and six *peculiar compounds*, all of which later researches have proved to be decomposition products formed during the analysis, and not pre-existent in the oil. He also stated that *acetic* and *butyric acids* were present, but the existence of these bodies is not fully confirmed by his analysis. Lastly, and in conformity with earlier analyses, he found the rest of the oil to be composed of margarin and oleïn.

These organic substances found by de Jongh comprised in all nearly 99½ per cent. of the oil, and it is a little surprising that *not a single one of them really exists in the oil*. The remaining half per cent. were *inorganic salts*, all well known from earlier examinations. De Jongh made quantitative determinations of them, but his results unfortunately were not particularly accurate. For instance, he found over 100 times more *iodine* than the oil actually contains. Of course it should be remembered that the analysis of organic compounds was then in its infancy, and the methods he employed were very faulty. He, however, gave his analysis the appearance of great exactitude (up to third and fifth decimals), and this for a very long time secured for his researches the reputation of a standard work.

Winckler (1853) found that the fatty acids were not combined with glycerin as glycerides, but with *propyloxide*; a statement which has not been corroborated by any of the later investigators, and which certainly is a mistake.

Down to 1869 the fatty acids of cod-liver oil were supposed to be margaric and oleïc acids, when Schaper found the former to be *palmitic acid*, with a small percentage of *stearic acid*. Stanford (1884) showed that iodine was present in a much smaller amount than had previously been supposed: he found the average percentage to be 0·000322. Buchheim (1884) proved that cod-liver oil does not and cannot contain any *biliary acids*. Allen and Thomson (1885) found that cod-liver oil contained *cholesterin*. Salkowsky (1887) pointed out that the well-known reaction with sulphuric acid is not due to the presence of bile-substances, as hitherto supposed, but to the simultaneous presence in the oil of cholesterin, fatty acids, and colouring matter ('*lipochrome*'). This particular pigment is found in cod-liver oil and palm oil, and a trace of it in cotton-seed oil, but in no other oil. Gautier and Mourgues (1888) found several alkaloïds in the darker oils, but not in those of a lighter colour.

We can now sum up the results of the analyses made up to 1888 by giving the following list of the constituents *said* by the various investigators to be present in cod-liver oil:—

| | Per cent. |
|---|---|
| Palmitin (fig. 877, p. 235) | 26 – 19 |
| Stearin (fig. 878, p. 235) | |
| Oleïn (fig. 879, p. 236) | 72 – 76 |
| Hydrochloric acid [1] | 2 – 5 |
| Phosphoric acid [2] | |
| Sulphuric acid [1] | |
| Formic acid [3] | |
| Acetic acid [2] | |
| Butyric acid [2] | |
| Valeric acid [4] | |
| Capric acid [4] | |
| Fellic acid [2] (p. 367) | |
| Cholic acid [2] „ | |
| Bilifellic acid [2] | |
| Gadinic acid [5] | |
| Physetoleïc acid [4] (p. 191) | |
| Morrhuïc acid [3] | |
| Delphinic acid [6] (fig. 672, p. 176) | |
| Iodine [7] | |
| Bromine [8] | |
| Potassium [1] | |
| Sodium [1] | |
| Calcium [1] | |
| Magnesium [8] | |
| Iron [9] | |
| Manganese [9] | |
| Gaduin [2] | |
| Bilifulvin [2] (p. 436) | |
| Biliverdin [2] „ | |
| Lecithin [3] (fig. 1,536, p. 435) | |
| Cholesterin [10] (p. 90) | |
| Phytosterin [10] „ | |
| Gelatin [1] (p. 436) | |
| Albumin [11] (p. 432) | |
| Ammonia [12] | |
| Propyl-oxide [13] | |
| Trimethylamine [13] (fig. 1,121, p. 315) | |
| Butylamine [3] (p. 440) | |
| Iso-amylamine [3] (p. 441) | |
| Hexylamine [3] „ | |
| Dihydrolutidine [3] „ | |
| Asseline [3] „ | |
| Morrhuine [3] „ | |
| Green soft resinous matter [1] | |
| Brown hard resinous matter [1] | |
| Peculiar comp. sol. in alcohol [2] | |
| Peculiar comp. insol. in alcohol [2] | |
| Four other peculiar compounds [2] | |
| Lipochromes [14] (p. 436) | |
| Other colouring matter [1] | |
| Smelling substances [1] | |
| | 100 100 |

According to these analyses the bulk of the oil (95–98 per cent.) consists of oleïn and the body, first described as margarin, afterwards corrected to palmitin and stearin. The existence of these acids, however, had never been properly determined by any exhaustive analysis; in fact, they had simply been permitted to pass down like heirlooms from generation to generation, and their identity had never been challenged. This is to be explained by the fact that there were no proper methods for isolating those fats: the constituents of which belong to the higher homologues of the aliphatic acids. For the determination of these it is indispensable that they should be in perfect purity, free from any admixture of higher or lower homologues, isomers, or acids with other bindings.

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[1] *Hufel. Journ.* 1837, p. 115; Brandes' *Arch.* vol. xxxii. p. 90; *Ph. Centralbl.* 1830, p. 17.

[2] De Jongh, *Disquisitio Comparativa Chemico-medica de Tribus Olei Jecoris Aselli Speciebus*, 1843.

[3] A. Gautier et L. Mourgues, *Les Alcaloïdes de l'Huile de Foie de Morue.*

[4] Benedikt, *Analyse d. Fette*, 1892, p. 369.

[5] *Jahresb. d. Chemie*, 1856, p. 490.

[6] *Geiger's Magazin*, 1828, p. 302.

[7] *Hufel. Journ.* 1836, p. 115.

[8] *Ann. d. Ph. u. Chemie*, xxxi. p. 94.

[9] *Pharm. Centralhalle*, xxx. p. 261.

[10] *Zeitschr. f. anal. Chemie*, 1887.

[11] *Pharm. Centralhalle*, xxx. pp. 10, 261.

[12] Wigger's *Hufem. Jahresb. d. Pharm.* 1869, p. 340.

[13] *Arch. d. Pharm.* cxxvi. (1853), p. 185.

[14] *Pharm. Centralhalle*, xxviii. p. 628.

Such, then, was the state of things when Heyerdahl commenced his investigations, which have occupied him uninterruptedly since 1880. The difficulties he has had to overcome have been formidable, for, at first, no systematic methods were available—only some isolated tests like Hehner's value, acid value, and bromine absorption were known, and these alone were not of much utility for the purpose. Since then, however, several others have been devised, such as saponification value (1883), iodine absorption (1885), and acetyl value[1] (1887). These, with their many ingenious applications, complementing and connecting the earlier methods, have established a system of analyses by which much valuable information may be gained. But although these tests give excellent results for saturated acids, and are serviceable in respect to the oleïc series, some of them turned out to be quite inapplicable in their original form to the acids of cod-liver oil, and a great deal of experimenting had to be gone through before modifications fit for use could be found.

The results of Heyerdahl's researches may now be briefly recapitulated. He could not find any oleïn or stearin in the oil, but he discovered two new glycerides, one of which, *therapin* (fig. 884, p. 237), is exceedingly interesting, and has already been described. The other and hitherto unknown glyceride is *jecoleïn*, containing jecoleïc acid (fig. 752, p. 193, and fig. 880, p. 236). This, like therapic acid, is an unsaturated acid, but with only one double bond. It belongs to the same series as oleïc acid, and is probably isomeric to doeglic acid. It is a very unstable compound—much more so than any of the other members of the same series. Heyerdahl succeeded in preparing the less unstable hydroxy-acid, which, however, breaks up in boiling water. He computes the amount of therapin to be 20 per cent. of the oil, and of jecoleïn, at least 20 per cent., but probably more. The rest of the glycerides he believes to consist of one or more unsaturated acids, belonging to the same series as jecoleïn, but hitherto unknown to chemists.

The only saturated acid that he could find was *palmitic acid*, and it was present to the extent of probably less than 4 per cent. Moreover, even this small percentage, actually found, was not detected in the 'stearin' at all, but in that part of the oil which remains fluid at a temperature of 7° of cold (centigrade). This is another interesting result of his researches: that the so-called 'stearin'—*i.e.* the fats of the oil that solidify at lower temperatures—contains neither palmitin nor stearin, but glycerides of, probably, new unsaturated acids—not yet determined. From this we may see that through the excusably ignorant demands of the trade, constituents of probably great therapeutical value are removed from the oil and literally thrown away.

*Rancidity of Cod-liver Oil.*—This is shown by Heyerdahl's researches to be founded, not upon free acids produced by the breaking up of the glycerides, but upon the formation of hydroxy-acids. There are free acids, to a slight extent, present in the oil when it is still in the liver of the living fish. Indeed, at that stage there is even more of the free acids present than there is in the steam-prepared oil, because some of these bodies are volatile and evaporate during the process of preparation. By exposing the liver to temperatures below freezing point the cellular tissues burst, probably because, under the influence of cold, they contract more than the oil. The oil then exudes, and in this way can be produced without the application of any heat, though not in commercial quantities. Heyerdahl found such oil to have an acid-value of 1·3, and of course there was no suspicion of it being rancid. By subjecting other exactly similar livers to the steam process he found that the oil produced at the beginning of the operation had an acid-value of 0·76–0·99; but at the end of the process this had diminished to 0·58–0·81, showing that some of the volatile acids had evaporated. In this oil also there was no rancid taste or smell. Further heating decreased the amount of free acids still more, but only to a slight extent; afterwards the acid-value began to rise slowly. After heating on a water-bath for five hours and a half, and at the same time passing 207 litres of air through the oil, the acid-value rose, although only to 1·22; but now the oil smelt and tasted disgustingly rancid.

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[1] The operation of these analytical tests is explained in the chemical part of this book, p. 241.

From this we may gather that *the free acids can have nothing to do with rancidity*, otherwise the acid-value would be proportionate to the rancidity. *The formation of hydroxy-acids is the true cause of the rancidity of cod-liver oil*, and it is more disposed to the formation of these acids than any other known oil. The difference in this respect between different oils and fats is, however, only one of degree. Olive oil, for instance, always contains hydroxy-acids, but they do not give rise to effects so unpleasant as those of cod-liver oil with the same acetyl-value. In fact, olive oils with—according to Heyerdahl's determinations — acetyl-values of 10·6–16·4 were very fair specimens of their kind, and when used for salad dressing were quite satisfactory. It is hardly necessary to add that cod-liver oil with similar acetyl-values would be very decidedly objectionable. Castor oil is a good instance of what hydroxy-acids are capable of; it is not, to put the matter mildly, a popular article of consumption, as indeed is pretty well proved by the fact that its chief patrons are those unfortunates who are still *sub ferula*. This failure to suit the popular taste is due to castor oil being by nature the glyceride of a hydroxy-acid, *ricinoleïc acid*. Its acetyl-value is as high as 153·4, even when the oil is in its purest state, and, of course, higher when it becomes rancid—or, strictly speaking, more rancid—by the addition of further hydroxyls.

It would seem that the more double bonds a fatty acid contains, the more easily do the hydroxyls attach themselves to it. Thus, cod-liver oil, which contains therapic acid with four double bonds, the highest number known, is very apt to become rancid. This aptitude, naturally, increases proportionally to the temperature, and although when well corked and kept in a cool place we have found the oil to keep in good condition for two years, it will, on the other hand, if left uncorked in a warm place, be entirely spoilt in less than a week.

The practical conclusions that we are entitled to draw from the foregoing are of very considerable importance to all who are in any way interested in the administration of cod-liver-oil. *The real value of the remedy lies in the fatty acids which it contains in the form of glycerides, and obviously the great point is to preserve these acids absolutely unchanged.* If they are altered the special advantages of the oil are thereby lost; and that is by no means all, for the hydroxy-acids which are formed from these peculiar fatty acids are not only of no value, but are actually injurious; for they make the oil nauseating to the taste and, what is far worse, they are very apt to set up gastric disturbances—of all things the least desirable in the majority of the cases for which cod-liver oil is prescribed.

It is no easy matter to preserve these acids unchanged, even when the best methods for doing so are adopted. They are, unfortunately, most unstable in constitution. Indeed, in the whole *materia medica* it would be difficult to find another body with a constitution so delicate as that of therapic acid, the most valuable constituent of cod-liver oil. It cannot even exist in the isolated state, and its little peculiarities in this way are perhaps hardly to be wondered at when we consider that its formation takes place in animals whose temperature never exceeds 5° C. A compound with similar constitution and properties could never be formed in warm-blooded animals or, in short, anywhere except where it is formed; and therefore it is hopeless to look for something to take its place. Nothing amongst all the other organic compounds, whether prepared by nature or in our laboratories, can possibly supplant the fatty acids of cod-liver oil.

*Preparations of Cod-liver Oil.*—The pharmaceutical preparations which have been made of cod-liver oil are remarkable both for their number and for a curious similarity in their life-history. That, in the case of most of them, is now complete, and it has been, briefly, an introduction with a great flourish of trumpets, a period of popularity, and—a niche in the museum of the curiosities of pharmacy. A selection descriptive of them will be found in an earlier part of this work. Here they may be dismissed with '*de mortuis nil nisi bonum*,' but concerning the preparations that have not yet 'joined the majority' a word or two may be added.

*Emulsions.*—Amongst them the *genus* emulsion with its numerous varieties stands at present first. The therapeutical justification for emulsifying cod-liver oil is said to be that a minute subdivision aids its absorption into the system. Some people, of course, might be inclined to ask if there is any proof that such aid is required—if the physiological emulsification of the oil by the intestine has ever been found deficient; also, supposing it has, can the deficiency be remedied by means of artificial emulsions? These emulsions are so different from nature's own that the best artificial subdivision of the oil results in globules which, compared with those seen in the intestinal epithelium, are like, say, Jupiter and his fifth satellite. Now, as the difficulty of subdividing fatty bodies may be said to increase in geometrical ratio to the fineness of the division, it requires some stretch of imagination to comprehend the advantages of an artificial emulsion which stops so far short of what nature requires. Again the fact remains that even the most 'elegant' emulsion will, after a time, break up, and separate the oil, and when it reaches a patient in this condition, a new but very different emulsion must be produced by following the well-known instructions, 'Shake the bottle.' This, however, is but one aspect of the question —the mechanical; the physiological and chemical yet remain. It is more than probable that *any* emulsion in passing through the stomach will be destroyed, as an emulsion, by the hydrochloric acid of the gastric juice before it can reach the duodenum. Further, supposing emulsions were merely useless, they might, *cæteris paribus*, be forgiven. But, unfortunately, the emulsification of an oil means accelerating the hydroxylation of the fatty acids, and for this reason: the subdivision of it enormously increases the contact surface by which oxygen can enter, and consequently increases the facility of forming hydroxyls: these are the bodies which cause disturbance of the digestive processes and the well-known and much dreaded cod-liver oil eructation. Of course the rancid taste of these oxidised fatty acids can easily be covered in an emulsion, but this tricks the palate only, not the stomach; here fine flavourings are of no use, for there are no nerves of taste, but there are nerves of equal sensibility, though acting in another way. They do not appreciate hydroxyls, and when hydroxyls are forced upon them there is trouble, the evidences of which are nausea, loathsome eructations, and so forth. Thus there seems to be but one conclusion to the question: even if all the *advantages* were proved up to the hilt, this one *objection*, the inevitable oxidation of the fatty acids, would in itself be quite sufficient to condemn all attempts at emulsifying cod-liver oil.

While, theoretically, the simple mechanical subdivision of the oil does not seem quite the thing required, its insufficiency is being practically proved by that great but slow teacher of man, experience. The result is a further 'advance': the addition of an adjuvant to the emulsion. Needless to say, the adjuvant is designed to help out the *hypothetical difficulty* in the absorption of the oil; another beautiful instance of how an idea, if once generally accepted, is handed down, heir-loom-like, from generation to generation, and never questioned. As a type of these adjuvants we may take 'pancreatin.' Here, again, the critical person would be disposed to ask, Is there any proof that the absorbability of cod-liver oil has been affected by a deficient pancreatic secretion, and if there is, can it be remedied by *this* 'pancreatin'? Of the four carefully set forth active elements of pancreatic juice, three of them, trypsin, amylopsin, and rennet have, as a matter of fact, no action whatever upon fats. The fourth is the yet rather hypothetical ferment, steapsin; and even if the existence of this in the pancreatic juice is granted, there still remains the reasonable question—is it present in the *dried* juice; and, should the answer be in the negative, then where does the use of 'pancreatin' come in? But should it be in the affirmative, it raises the further question—what does steapsin do? On the showing of its own advocates its action must result in splitting off the therapic acid, the existence of which as a free fatty acid in an emulsion is simply impossible. It would, in accordance with the conditions present, either break up altogether or undergo conversion into the thing evil—an hydroxy-acid. Finally, the vehicles necessary for preparing artificial emulsions are not always therapeutically expedient; they are quite unnecessary, and therefore undesirable additions to our *materia medica*.

All these considerations lead us to one conclusion—that there is no really valid reason for the existence *of artificial emulsions*, but that there seem to be obvious reasons for their non-existence. Other considerations tend to the conviction that there is no need of artificial aid of any sort, because nature is capable of undertaking the work herself, and does so, to perfection in the *physiological emulsions* she prepares; the elements necessary for the natural, that is the perfect, emulsification being provided by nature, *exactly where and when* they are required, and in a quantity which, so far at least as cod-liver oil is concerned, is apparently always amply sufficient. These elements may be classified roughly as the mechanical and the chemical actions. Concerning the former no more need now be said than that, compared with the pestle and mortar, 'it grinds exceedingly small,' but concerning the latter, some further explanation may not be out of place.

It is a most interesting fact, as bearing on the medicinal virtues of cod-liver oil, that it differs from all the other fats with which we are acquainted in respect to the ease with which it can be emulsified in the presence of the two chemical bodies fresh pancreatic juice and glycerin, without the aid of any gum whatever. Nature provides the former, and we may reiterate that there is no real evidence regarding an insufficiency in her supply; the latter can never be insufficient, because it is provided by the oil itself, in which it is present in the precise quantity required. The secretion of the pancreas comes in contact with the oil, not in the stomach, where the acid fermentation would render its action futile or perhaps, indeed, totally destroy it, but in the duodenum, from which downwards through the jejunum and ileum all the conditions are in its favour. Under these circumstances, the fresh pancreatic secretion by its action upon the oil provides the other necessary element, the glycerin.

Nature herself seems to enforce the lesson, if we would let her, that by means of the pancreatic juice *she* provides, and the glycerin of the oil, such an emulsion is produced *in* the human economy as it is hopeless to look for *outside*, however skilful our manipulations.

After all, the most astonishing circumstance connected with artificial emulsions is, that so much labour and thought should have been bestowed upon overcoming a hypothetical difficulty of assimilating the oil, when all the while no one was believing in the therapeutical value of these very same fats, and therefore not attaching the least importance to them. The valuable part of the oil was always considered something distinctly separate from its fatty constituents, and learned men and grave professors have occupied themselves with hunting after this 'something,' only to find it, like a phantom, suddenly disappearing before their eyes just when they thought they had grasped it. This will-o'-the-wisp is the so-called 'active principle,' and on account of the extensive use made of this catch-word we cannot dismiss the subject with a mere passing notice.

*Active Principles.*—The effect of cod-liver oil on the system is so different from that of any other oil, that science has subjected it to all sorts of torture in order to make it reveal its secret. This the poor oil was, of course, quite willing to do had it been properly asked. The inquiries, however, were always wrongly directed. From 95 to 98 per cent. of the oil was supposed to be ordinary fat, and quite unworthy of any special attention. The whole of the examination and cross-examination was therefore turned upon the remaining two to five per cent. It is astonishing what a number of things were found in this small quantity, as may be seen in the lengthy list on p. ci, all of them being 'chaperoned' by scientific men of distinction. It is difficult to imagine that any of them could have an important influence upon the action of the oil, for those that are, without doubt, present are so in homœopathic doses only; the percentage of some, indeed, cannot find expression before the third or fourth decimal. Yet nearly every one of them has in turn been represented by its discoverer, or someone else, as '*the active principle*' of the oil, and has served as the basis for substitutes intended to do away with cod-liver oil entirely. Volumes have been written on this, scientists have lectured upon it, enterprising pharmacists have prepared it, sold it, and presumably profited by it, and yet it does not exist; the oil, however, still exists, and in a fairly flourishing condition, while its proposed substitutes are either resting in the aforesaid 'niche,' or seem likely to do so at an early date.

Such a result is not surprising if it can be demonstrated that this two to five per cent. of odds and ends has nothing whatever to do with the therapeutical value of cod-liver oil; and we think that some further considerations will lead to the conclusion that such is the case.

By far the greater number of the remedies used in medicine act by the physical or chemical influence which they bring to bear upon the tissues of the body. Cod-liver oil, on the other hand, is one of a much smaller group of *materia medica*, which act, not by influencing the tissues, but by becoming part and parcel of them; in other words, they are simply food substances, which, in one way or other, possess special advantages distinguishing them from other and ordinary foods, and justifying their adoption as therapeutical agents. No active principles are to be expected in the members of this group, and to attempt to find some such body in cod-liver oil is just as likely to be succesful as would be an endeavour to find an active principle in—say bread.

It is indeed, at first sight, surprising that anyone should have thought that cod-liver oil could contain an active principle, but for this, as for most things, there is a reason. The abstract idea of what should be the properties of a medicinal substance is naturally derived from the properties common to the great bulk of such substances, and as most medicines act in the way we have described, it is obviously quite possible for them to possess 'active principles'; indeed, as a matter of fact, the majority of them do. But although the majority of drugs have an active principle, it is logically ridiculous to deduce that *every* drug must have such a principle; yet this is exactly what is done by many people, and, combined with the ingrained misconception of the nature of the fatty constituents, is the explanation of the absurd belief in, and the unavailing search for, an active principle in cod-liver oil.

We have said that the search was unavailing, but that is, perhaps, hardly the correct way to put it, for whenever a search has been instituted it has been successful, only each different investigator has happened to find a different 'active principle.' This is rather unfortunate, for of course the latest discovery is the real active principle—until such time as another one is found. Like the men who discover them, the fame of these valuable principles is somewhat transient—here to-day and gone to-morrow; yet one thing always remains—cod-liver oil.

For centuries this oil has been used and esteemed by all the nations able to obtain it. Many of them had no communication with each other: the inhabitants of North America did not learn the virtues of cod-liver oil from the inhabitants of Northern Europe, or *vice versâ*, but the various peoples in each of those regions learned the lesson from their own individual experience. Cod-liver oil, it is to be noted, was not the only, or even the most easily obtainable, oil or food, and yet every one of these primitive peoples selected it, and it only, being taught by experience that it was quite different from, and much more valuable than, other oils or food substances. Here, then, we have the process of 'natural selection' by which cod-liver oil was separated from, and esteemed above, other and similar products; and this was done, not in one region only, or by one people only, but in several different and widely separated regions, and by different and altogether disconnected peoples. As we have said, the oil could not have been originally the one thing, or even the most likely thing, 'in the running'; but when we find that from its rivals it, and it alone, was selected, and this in places so far from each other as Norway and North America, and by nations so different as the Laplanders and the Alaskan Esquimaux, we are forced to come to the conclusion that there must be something special in the oil—something not to be found in other substances—but this something is not an 'active principle.'

If there really were an active principle in cod-liver oil, we might be pretty sure that it would have been discovered long ere now. In the case of other medicinal substances, the active principle: alkaloïd, glucoside, acid, or anything else, has been discovered and separated; its chemical composition has been determined, and its physiological action has been investigated and settled, and there the matter has ended. In no case has another and different active principle been found to explain the value of the drug; in no case has an active principle totally disappeared from the ken of man after it has been discovered, investigated, and established; in no case, in fact, do these things happen—except in the case of cod-liver oil, where they all happen; and *the* active principle of to-day is the knell of *the* active principle of yesterday. We are, in consequence, forced to the conclusion either that the active principle of the oil is something different in every way from all other active principles, or, what is more likely, that no active principle exists.

Heyerdahl has been the first to direct his inquiries to the fatty constituents, and their reply to his attentions has been prompt and to the point. His researches are important in respect to their practical results and of great interest in regard to the theoretical conclusions that may be drawn from them concerning the active principle of cod-liver oil.

The idea that this principle is to be discovered somewhere outside the glycerides may be safely discarded. When it is remembered that the chief property of cod-liver oil is to build up, and strengthen, the system it appears almost ridiculous to look to infinitesimal fractions of well-known compounds for the explanation of that building-up property. These fractions are not even perfectly innocent in their nature. For example; Gautier and Mourgues, found in the light-brown oil minute quantities of some two or three alkaloïd-like poisonous compounds, over which no little fuss was made, as they, also, posed in the character of the latest ‘active principle.’ They have been classified by their discoverers as ‘leucomaïnes,’ that is to say, as products of katabolism, formed during life and through the ‘vital forces’ that sustain life and *in casu* in the livers of the living fish.

This must surely be a mistake; if it were true, there could be no reason why these alkaloïds should not be found in all sorts of cod-liver oil. But according to the investigators themselves the bodies in question do not occur in the steam-prepared oil, and it is only in the light-brown oil that they are present in a quantity (0·2 per mille) sufficient for chemical examination; while, again, they are altogether absent in the brown oil. Heyerdahl found them just traceable in the pale oil as detailed by him in the preceding pages.

The following are facts on which all agree, and in the opinion of the writer they are very striking. In the oil extracted from fresh livers there are no alkaloïds; in the oil drawn from decayed but still comparatively fresh livers there are traces of them; in the oil skimmed off whilst the putrefaction is in full swing they are plentiful; in fact, the greatest quantity occurs; in the brown oil, which has been exposed to a temperature of 120° to 150° C., there are none; all of which seem to point to these alkaloïds being really ptomaïnes formed by bacteria from putrefying albuminous substances of the liver.

In the case of steam-prepared oil the bacteria have no opportunity of commencing their work on account of the relatively high temperature at which the oil is prepared, and also, because the exuding oil forms a protective covering all over the hepatic tissue. But no sooner is the oil drawn off than the bacteria commence action upon the unprotected liver-rests, as is quickly evidenced by a stench which, even within an hour if the temperature happens to be favourable, may become so strong as to be almost intolerable.

In the case of pale oil when the livers are heaped in a barrel, only those that come to the surface are attacked, the rest being protected by the exuding oil. Gradually, however, as this is drawn off, more and more of the livers become exposed to the air, and when the process has proceeded so far that the light-brown oil is being formed the bacterial activity becomes very lively, as manifested by the same intolerable smell.

Finally, at the temperature at which brown oil is made, these bacterial products are decomposed or volatilised, and therefore they are not found in this particular variety.

The ‘liver-rests’ (*Graxe*) consist for the most part of albuminous substances, and when not under the protecting cover of the oil the rapidity with which they are attacked by bacteria is simply astounding, and it is very difficult to prevent, or put a stop to, the bacterial destruction. We have tried sulphurous acid and carbon-disulphide, but for practical purposes they were useless; and carbolic acid, sublimate, and similar disinfectants cannot be used, as the liver-rests are employed as manure.

Curious misunderstandings have arisen from an ignorance of this property of the hepatic tissue: its extreme susceptibility to bacterial influence. Thus a paper was lately read before l'Académie des Sciences, Paris, in which the author states that the alkaloïds of cod-liver oil are all of biliary origin, and goes so far as to assure us that this can easily be proved by the following proceeding! After a small slice of fresh liver tissue has been snipped off and carefully disinfected, it is left for two or three hours under a desiccating bell jar, after which plenty of microscopical crystals of alkaloïds are to be found. This is the process of stopping the chinks and leaving the door wide open—of course, after those two or three hours under the bell jar it would be surprising if abundance of ptomaïnes were not found.

These alkaloïds, therefore, cannot be considered as normal products in the light-brown oil, but are undoubtedly impurities with which the oil has been contaminated by the putrefaction of the liver. They are powerful poisons, and have, of course, a therapeutical effect upon the system; but—not the wonderful building-up and strengthening action which is the characteristic of cod-liver oil, and which the varieties of the oil without ptomaïnes manifest at least as well—and need we add quite as safely?—as those varieties that do contain such 'adjuvants.'

Now, however, when we have Heyerdahl's discoveries before us there is no need to search for some mysterious 'active principle' amongst the 5 per cent. of odds and ends. These, to be concise, are not normal constituents of pure cod-liver oil, inasmuch as valeric, capric, and gadinic acids, gaduin, ammonia, trimethylamine, alkaloïds, and such substances are partly decomposition-products, formed in the hands of the analyst whilst conducting his operations, and partly products of bacterial activity after the oil has left the hepatic cells. They exist only in one special kind of oil, in the preparation of which opportunity for bacterial putrefaction has been given.

Cod-liver oil is really much more a food substance than a medicinal substance, and to expect it to contain an 'active principle' in the true sense of the term is little less than absurd; its therapeutic value depends, certainly not on any active principles, but on its remarkable efficiency as a nutritive agent. It is, then, much more rational to look to the newly discovered acids, which constitute 95 per cent. of the oil, as being the probable basis of its therapeutic value.

The chief function of the absorbed fats in the economy of the organism is to form compounds from which the system can, in the most effective way, be supplied with the necessary income to cover its expenditure. Of such compounds, forming a store from which the organism is incessantly drawing supplies of repairing materials and which in themselves provide all the necessary elements—phosphorus, nitrogen, carbon, hydrogen, and oxygen—*of these we know only two, protagon* and *lecithin.* When more fat is absorbed than is necessary for forming these two compounds it is deposited as fat, and in the adipose tissue, without any intervening link.

Protagon and lecithin are analogous compounds; the structure of the former, which is largely found in the brain, is very complex and not fully known. This much, however, has been ascertained, that it can be split up into two compounds, *cerebrin* and *kerasin*, probably glucosides, and that *lecithin is a constituent of both.* The structure of lecithin, on the other hand, is fully known (*vide* fig. 1,536, p. 435). It is composed of phosphoric acid to which a nitrogen compound, choline, is linked on one side, and a glyceride on the other. Further, it has been found that the glyceride is not always the same: sometimes it consists of two similar acid radicals, sometimes the two are quite different, *evidently depending upon the kind of fat that was at hand at the time of formation.* Lecithin originates in plants, and from them it enters the animal organism, where it is found *in every growing cell.*

As lecithin is practically ubiquitous in foods it arrives in the stomach in company with nearly everything we eat, and even with cod-liver oil. It is not affected by the gastric juice, but when it reaches the intestines it shares the fate of cod-liver oil; the pancreatic juice, or rather the hypothetical steapsin, splits it up into its constituents, glycero-phosphoric acid, free fatty acids, and choline. All these bodies pass through the striated surface of the epithelial cells, and are then taken up by the lymph-corpuscles—cod-liver oil, it is to be noted, is taken up just in the same manner. A regeneration of the lecithin takes place within the lymph-cells, which then discharge it into the lacteals.

When fats and lecithin are taken simultaneously in the food, as they almost always are, they meet in a disintegrated state in the lymph-corpuscles, that is, as free fatty acids of various kinds, corresponding to the fats partaken of, and as glycero-phosphoric acid, glycerin, and choline, or perhaps a derivative of the latter.[1] Then the regeneration of lecithin is commenced in the lymph-corpuscles, and there can be no doubt that glycero-phosphoric acid *makes a selection from the fatty acids now within its reach*, and without any regard to the connections of its former existence. If it picks out those acids which are best fitted for its new duties, that is only what we would expect it to do, in harmony with all the genetic laws within our knowledge—for instance, the selecting activity of secreting cells. Its new duties are to give off to the blood the material that is required for the maintenance and renewal of the body. For this purpose it is embodied with the protoplasm of the cell, and when the blood arrives there, its oxyhæmoglobin gives off its oxygen by which an actual breathing process of the protoplasm is maintained, resulting in the breaking-up of lecithin and other of its constituents into various compounds, which are carried away with the blood and deposited at the places where they are properly required.

Now, unless the above, which is founded on the latest physiological data, is utterly wrong, the extraordinary facility with which therapic, jecoleïc, and perhaps other acids of cod-liver oil break up under the influence of oxygen makes it obvious that they are, collectively, the very thing required for the easy nutrition of the body. By them the work of building up and strengthening the system can be accomplished with the least expense of energy, and it seems almost impossible that the lecithin should select any other acids than these for its regeneration.

This simple and plain theory may be expressed in few words—the active principle of cod-liver oil is the oil itself.

*Recapitulation.*—The reputation of cod-liver oil was established many centuries ago and, indeed, probably in prehistoric times. It was no reputation built up by adventitious aids; no perfectly disinterested scientist discovered the virtues of the oil, and forthwith advertised them—for the benefit of suffering humanity. The oil, in fact, made its own reputation, or to put the matter somewhat more accurately, it was discovered, advertised, introduced, and established in favour by 'natural selection,' and it is notable that this took place, not in one country only, or amongst one people, but in several widely separated regions of the globe and amongst several totally disconnected races. The reputation of cod-liver oil was thus 'made and guaranteed' by nature herself, and as civilisation opened the means of intercourse between different countries, the use of the oil spread from the regions of its origin, till at the present day it has become practically universal. Here a very natural question may crop up: if cod-liver oil is so excellent, why all the attempts that have been made to aid its action by adding this thing or that to it, or by making it into something different from what it is? A study of the history of these attempts supplies an answer, for they can all of them be traced back to one and the same starting-point—an endeavour to overcome the difficulties in administering the oil.

These difficulties were really serious, as anyone with experience, especially personal experience, of the matter will admit. The oil, as hitherto known, possesses sometimes a far from pleasant taste, always a tendency to disorder the digestion and to cause the much dreaded repeating. It was with the praiseworthy object of overcoming these drawbacks that the 'preparations' of cod-liver oil were started, but unfortunately in directions that were not in the least likely to lead to success.

The drawbacks are due to certain impurities which are, or, as we ought now to say, were, found in the oil. Now, even from the *a priori* point of view, there does not seem to be much chance of success with these preparations by merely covering the impurities, no matter how skilful the pharmacy employed. In fact, there is only one way to success in the administration of the oil, and that is, not by *disguising* but by *excluding* the impurities; and we use the word 'excluding' advisedly, because *once* the presence of the impurities is permitted, *removal* is impossible; it follows, therefore, that an inferior cod-liver oil *cannot be refined*, and to speak of steam *refined* oil shows a complete ignorance of the subject. The impurities are of two kinds. First, the decomposition products of albumen which are derived from the putrefaction of the liver tissues, and which naturally give the oil a most repulsive taste and smell. Secondly, the objectionable products from the oil itself formed by the oxidation of the free fatty acids, which are the cause of the nauseous repeating.

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[1] Glycero-phosphoric acid, and recently also neurine, a derivative from choline, have been found in the blood, both in the free state (*Ber. d. d. chem. Gesellschaft*, xxvii. Ref. 420).

The first step towards the exclusion of these impurities was the invention and introduction of Peter Möller's 'steam process.' The oil prepared by this is absolutely free from decomposed albumens, if the process is properly carried out. It does, however, contain, more or less, the oxidised fatty acids, and therefore even the very best steam-prepared oil is apt to cause repeating. The second great step towards the production of a pure oil has now been accomplished. The results of our chemical investigations show that the fats of cod-liver oil are entirely different from other fats, and that one of their most remarkable characteristics is a much stronger tendency to form hydroxylated compounds than that possessed by any other fatty substances. Our knowledge of these chemical and physiological properties, acquired through Heyerdahl's interesting researches, forms the foundation of our new process, based upon the principle of *prevention*.

It was found that the only practical method by which the hydroxylation of the free fatty acids could be prevented was by their complete isolation from the action of free oxygen throughout the whole process of preparing the oil. This is done in the process which we have devised by keeping the oil under an atmosphere of carbonic acid from beginning to end—from the moment when it leaves the liver cells till it is safely bottled and corked. Hydroxylation is thus impossible, and the oil is not only odourless and tasteless but it is *absolutely hydroxyl-free, and therefore does not cause unpleasant repeating.* It is, in short, the ideal cod-liver oil, for it contains the maximum of the therapeutically valuable constituents and the minimum, or more precisely none, of the objectionable constituents. This, of course, is only when the oil is fresh, for in time the fatty acids must become oxidised, no matter how well they may be protected, and it is for this reason that we insist on the importance of never using any oil older than that of the previous year's fishery. These remarks may be concluded by a short statement of the conditions that we would lay down as *essential* for the preparation and administration of medicinal cod-liver oil. First, the livers should be those of cod-fish only, and those from any other source rigidly excluded. Secondly, the livers should be perfectly fresh, and any that have been kept, or that betray the slightest sign of decomposition, should be rejected. Thirdly, livers showing any indication of disease or derived from diseased fish should on no account be used. Fourthly, in extracting the oil the livers should not be exposed to a high temperature, and to the proper temperature for just the necessary time only. Fifthly, from the beginning of the process of extraction till it is safely corked up in bottles, the oil should never, even for a moment, be permitted to come in contact with the atmosphere or with free oxygen in any form. And lastly, a good oil should never be mixed with other drugs beforehand. It may be done *immediately* before being taken, but it is far better, when their employment is considered necessary, to give them separately.

# II

# THE LAW
OF
# ATOMIC LINKING

DIAGRAMMATICALLY ILLUSTRATED

BY

F. PECKEL MÖLLER, PH.D.

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# ABBREVIATIONS

Amer*ican* Ch*emical* J*ournal*

Amer*ican* Journ*al of* Pharm*acy*

Ann*alen der Chemie und Pharmacie*

Arch*iv* d*er* Ph*armacie*

Arch*iv für* exp*erimentelle* Patholo*gie und Pharmakologie*

Beilst*ein*, *Handbuch der organischen Chemie*, $2^{te}$ *Aufl.* 1886–1890

Benedikt, *Analyse der* Fette $2^{te}$ *Aufl.* 1892

Ber*ichte der deutschen chemischen Gesellschaft*

Berl*iner* klin*ische* Wochenschrift

b*oiling* p*oint*

B*ritish* P*harmacopœia*, 1885

Centralbl*att* f*ür* Bacteriolo*gie und Parasitenkunde*

Ch*emical* N*ews*

Ch*emiker* Zeitung

Ch*emist* & D*ruggist*

Compt*es* rend*us des séances de l'académie des sciences*

D*eutsche* Med*izinische* Wochenschrift

Halliburton, *Chemical Physiology and Pathology*, 1891

Heger, Synopsis *der neuen Arzneimittel*, 1891

Journ*al* d*er* russ*ischen* ch*emischen* G*esellschaft*

Journ*al für* pr*aktische* Ch*emie*

J*ournal of the* Ch*emical* Soc*iety*

Lauder Brunton, *Introduction to Modern Therapeutics*, 1892

Med*ical* Ann*ual*

Med*ical* Mag*azine*

m*elting* p*oint*

Merck's Ber*ichte*

Meyer, Jahr*buch der Chemie*

Monatsh*efte für Chemie*

Monatsh*efte* f*ür* pr*aktische* Dermato*logie*

Ph*armaceutische* C*entralhalle*

Ph*armaceutische* Zeitung

Ph. B. = *British Pharmacopœia*, 1885

Pictet, *Die Pflanzenalkaloïde*, 1891

Proc*eedings of the* Chem*ical* Soc*iety*

Repert*orium* d*er* Thierheilk*unde*

R*oscoe* & Sch*orlemmer Organic Chemistry*, vol. i. 1885, vol. ii. 1890, vol. iii. 1891, vol. iv. 1888, vol. v. 1889, vol. vi. 1892

Schaedler, Technolo*gie der Fette und Oele*, 1892

Therap*eutische* Monatsh*efte*

Wiener med*izinische* Bl*ätter*

Wiener med*izinische* Presse

Z*eit*schr*ift* f*ür* klin*ische* Med*izin*

Z*eit*schr*ift für* physiolo*gische* Ch*emie*

Temperatures are given in Centigrades unless otherwise stated.

*Errata*: page 53.—Line 2, *for* terpenes *read* camphenes.
„ 98.—Under Fig. 437, and wherever else the name terpine-hydrate occurs, *read* terpine *only*.
„ 109.—Last line, *for* metoxyl *read* methoxyl.
„ 120.—Second line of title under Fig. 503, *for* *p*-position *read* *m*-position.
„ 147.—According to *Ann.* cclxxx. pp. 1–35, *Ber.* xxvii. *R.* 650, the structure Fig. 607 belongs to chrysazin, and that of Fig. 609 to iso-anthraflavic acid: Fig. 605 would then represent frangulinic acid.
„ 294.—First line of text under Fig. 1050, *for* Seven *read* Four.
„ 308.—First line of text under Figs. 1093, 1094, *for* o-di-nitrol-cresol *read* *o*-di-nitro-cresol.
„ 314.—Bottom line, *for* p. 351 *read* p. 352.
„ 335.—Third line, indulines are not azo-compounds but belong to diazines (p. 389), and may be considered derivatives from pyrazine, Fig. 1402.
„ 367.—Third line in text under Fig. 1305, *for* fellinic acid *read* fellic acid.
„ 397.—Second line of text under Fig. 1431, *for* $(CH_3)_2$ *read* $C_2H_6$.
„ 397.—Third „ „ *for* $(CH_3)_3$ *read* $C_3H_9$
„ 483.—Fifth line from bottom, Vaubel's formula is also termed Marsh's formula.
„ 492.—Twelfth line, *for* p. 88 *read* p. 108.

One of the difficulties barring the royal road to Chemistry is the nomenclature—the veritable skeleton in the chemical cupboard. In this respect Chemistry might well be compared to a huge metropolis built, after the olden style, on no principles whatever. A city with innumerable tortuous streets named sometimes to indicate their point of starting, sometimes their destination, sometimes misleadingly neither, and many of them further boasting of several names, while others share a single name in common. A city, moreover, inhabited by people of all nations, each making 'confusion worse confounded' by insisting on naming the streets in their own tongue and after their own sweet will. A city in whose bewildering labyrinth even the most experienced often finds himself astray, and over whose gates the stranger ought to see DANTE'S warning words, '*Lasciate ogni speranza, voi ch' entrate.*'

To introduce order into this chaos is no easy task, but some day it will have to be done, and the present generation, always anxious to show its good intentions, has made the first move in the matter by convening the Congress of Scientists which met at Geneva in April 1892. The Congress proceeded to consider a scheme that had kindly been provided for its guidance, but it soon became evident that the rules laid down in this had been framed exclusively for the convenience of the French nomenclature, and no regard paid to that of '*les autres là bas*,' and that some of the propositions set forth in it could not bear their own consequences. In fact, the committee that drew up the scheme had worked on a principle suspiciously related to '*après nous le déluge*,' or, in English, *we* press the button, *you* do the rest. No resolution which may be taken as final was passed (see *Nature*, May 19, 1892, p. 57), and we now wait with great patience and small expectations for another Congress.

Nomenclature thus seems hopeless for the present, but fortunately it is not everything. We cannot quite say 'what's in a name,' but certainly the mere names of things chemical are of little importance compared to an actual knowledge of the things themselves. Chemistry, as we know it, is a very young science, and the older generation had little opportunity of studying it. The younger generation, on the other hand, have to learn a mass of Chemistry, for examination purposes; but how much of it do they retain in after years? They have to cram so many things that are utterly useless that they have no time to get a proper understanding of useful things; and this *proper understanding* is in Chemistry, of all subjects, the one essential—the one gateway to the path of knowledge, 'and few there be that enter therein.' How many, for instance, of those who study Chemistry as a subordinate branch of knowledge ever form a real mental picture of the formulæ about which they read? Yet without that, a proper understanding of the subject can never be arrived at—with it no science is more easily understood than Chemistry.

Bearing this in mind the writer has abandoned the orthodox but somewhat unedifying method of representing chemical formulæ, and has introduced a new system of diagrammatic illustrations. A defence of this system is laid down in the latter part of the treatise; but here it may be remarked that this, in common with all pictorial methods of representation, has to serve two almost irreconcilable masters—strict adherence to the truth and practical usefulness. A little of the former has perforce been sacrificed for the sake of the latter, but in no case have any of the *main features* of the subject been interfered with. The diagrams do not profess to represent the theory of atoms in space, but they are eminently suggestive, if assisted by a more extensive knowledge of Chemistry than can be presented in these pages. For the purposes of this book, however, their intelligibility is their sole virtue, and by means of them a glance will lay bare to the eye of a novice the whole details of the constitution of even the most complicated compounds, to grasp which, when represented in the ordinary way, might rack the brain of a *savant.*

In addition to these pictorial representations, the following pages contain some new things of a different nature—statements and theories for which the writer has the misfortune to be responsible, and the estimation of which he must leave to his readers.

The material for the treatise has been selected chiefly to meet the interests of the medical profession, and much, therefore, which is found in the ordinary books on Chemistry has been omitted, while much which is not found in them had to be admitted. The traditional arrangement of the subject matter has also been considerably altered. As in a pack of cards, which may be arranged either according to value in kings, queens, &c., or according to suit in spades, clubs, &c., so, here there are two methods, each having its advantages and disadvantages. That which has been adopted is the more natural of the two, as it does not split up the matter quite so much, and it almost entirely obviates *the necessity* of referring, in the earlier parts, to subjects with which the reader will not become acquainted until later.

The description of physical properties has been limited chiefly to their boiling- or melting-point. This sufficiently suggests their state of aggregation, and further description would be of but little real advantage unless very much detailed. With few exceptions the practical preparation of compounds has not been entered upon, because the much tried patience of medical men need not be burdened with things chiefly of interest to the chemist.

The authorities have been given in all cases where the statements are doubtful, or do not occur in ordinary text-books, either because they are outside the scope of such books or because they are of too recent date to have as yet found a place in them. The only exceptions are some therapeutical notes which have been culled from the *Medical Annual*, HEGER'S *Synopsis der neuen Arzneimittel*, and LESCHER'S *Recent Materia Medica*: where the original authorities will be found.

# CHEMISTRY

> Non videri absurdum concipere, in prima mixtorum corporum productione, materiam illam universalem, ex qua ea inter ceteras universi partes constabant, in exiguas particulas, diversis magnitudinibus et figuris instructas, varicque notas, actu divisas fuisse.—Robert Boyle, *Chymista Scepticus*, Part I.

Curiosity is our common inheritance from Mother Eve. When our children break up their toys and dolls to see what is inside we call their curiosity destructiveness; but when we see the venerable scientist, with his flasks, tubes, and chemicals, split up everything round him we call it search for the truth. Essentially there is no difference between the two, though there is a distinction: the child sees at once the truth; the scientist will never know the ultimate truth, however near he may at last approach it.

When we, in search of truth, have collected a number of facts we try to explain them by devising a theory; this passes as truth until new facts present themselves contrary to the theory obtaining at the time. We cannot ignore the facts, and stick to the old truth and say, with Tom Brown, 'So much the worse for the facts'; there is nothing else to do but to discard our former truth and look about for a better one.

So in chemistry we have had successively Berzelius' electro-chemical theory, Liebig and Wöhler's radicals, Dumas' substitution, Laurent's nucleus, Gerhardt's types, with interpositions by the researches of Dalton, Avogadro, Wollaston, Gay-Lussac, Dulong and Petit, Cannizaro, Mitscherlich, Faraday, Clausius, Maxwell, Boyle, Williamson, Odling, Wurtz, Kekulé, and many more.

To go into details of these theories is beside our purpose. There is, however, a distinction between them and the more modern ones which have been not only a turning-point in their succession, but has also opened immense tracts of new fields and fresh pastures for the ever-busy workers in the organic chemistry world.

Before this distinction can be properly understood it is necessary to explain what, in the present day, are the accepted meanings of the words *atom* and *molecule*.

Experiments and observations have from time immemorial led our intelligence to the conviction that nearly all things we see around us are compounds of other bodies, which bodies were termed elements long before any real element was discovered, or at least recognised as such; and the endeavours of scientists from Empedocles' time have been to find out what these elements are out of which the whole world is formed. In order to decompose these compounds a force is necessary; but besides fire the only one known in Empedocles', Plato's, and Aristotle's time was the mechanical force. Before the era of dynamite and kindred productions of civilisation mechanical force was of no avail; a piece of sugar persistently remains the same sweet thing, however much it may be ground and finally divided. Therefore the old wise men were left to philosophical speculations, and found out that there were four elements: two heavy, earth and water; and two light ones, fire and air; with a fifth one (*quinta essentia*) in reserve, but vaguely described as ether, among the alchymists designated as the philosopher's stone.

Gradually, as we learnt to know and to use other forces, such as heat, chemical force, electricity,

&c., these were employed, and we succeeded in splitting up everything in the universe, including the sun and other fixed stars, into altogether sixty-nine separate and distinct bodies (exclusive of some dubious ones), each of which it has not been possible by any, at present available, means to divide further into others with differing qualities. These are what since Boyle's time (1627–1691) we understand by *elements*.

Now, if we take one of these elements, a piece of coal, for instance, we can, of course, cut it, and finally grind it in order to divide it into the smallest particles possible. Practically there is a limit when any amount of further grinding can make it no finer; but even theoretically there is a limit to its divisibility. Both physical and chemical phenomena and reactions tend to demonstrate that a piece of coal or any other element one cubic line in size having been divided into some trillion equal parts, further division is impossible. Mentally, of course, we could go on dividing as long as we like, but practically it would be impossible.

These small particles are called *molecules*. Any one of them is in all respects as good coal as the larger piece from which it is separated.

Though not divisible mechanically, it is still possible to divide each molecule of an element through other forces, some in two, others in more, for each element equally large and weighty particles. These ultimate particles of an element are called *atoms*. Their characteristic quality is that they cannot ordinarily exist in the free state by themselves; as soon as they are set free they combine with other atoms and form molecules.

It is generally admitted amongst scientists that the atoms are really not the ultimate particles, only we have not yet found the means of the further division, which would then simultaneously be both a quantitative and a qualitative one. Many go so far as to advance the hypothesis of one common primitive matter, from which, by different quantities and mutual arrangements, the atoms of the several elements are formed.

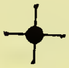
Just as we have demonstrated the division of *elements*, we can mechanically divide any *compound* body until we come to the molecule, which is not further divisible by that means. Calling, however, other forces to our assistance, we can split up the molecule into atoms of the different elements of which the compound consists, and these will assort themselves, and then combine to form molecules of the different elementary constituents. It must be remembered that the molecules are so minute that there is never any question of treating a single molecule; in the smallest quantity of a compound, one cubic line, for instance, which practically can be treated by chemical means, there are some trillions of molecules. If, therefore, we take one single drop of, say, *carbon disulphide*, which is a fluid, we have to treat so large a number of molecules at the same time. Every molecule of this compound consists of one atom of carbon and two atoms of sulphur. We can separate them, but as soon as they are set free atoms of carbon from one molecule combine with atoms of carbon from other molecules, and form molecules of carbon; atoms of sulphur in the same way combine and form molecules of sulphur; so atoms cannot exist alone, but must form molecules.

The first quality of the atoms taking our attention is their ability to unite mutually. The exact nature of this faculty is not fully known, but it may be regarded as a force by which the atoms bind one another together. It has been found that an atom of *hydrogen* cannot combine with more than one other atom of any sort. We therefore look upon the atoms of hydrogen as possessing this force of combination only once. If we take an atom of another element, and charge it with as many atoms of hydrogen as it will accept, we naturally conclude that that atom has as many forces of the same quality as it has accepted atoms of hydrogen.

An atom of *carbon*, for instance, is capable of uniting with four atoms of hydrogen and no more. We therefore regard carbon as an element whose atoms are possessed of four of these forces. An atom of *oxygen* can combine with two (but no more) atoms of hydrogen; consequently it must have two similar forces.

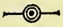
In order to illustrate this graphically we may represent a carbon-atom as a black disc upon whose circumference the four forces are represented as four equidistant and equally long lines, bristling like iron-filings on the pole of a magnet, still able to turn in all directions as if fixed to the atom on pivots; an atom of oxygen as two concentric circles provided in the same manner with two lines; and an atom of hydrogen is represented by a smaller circle whose single force is fixed in the form of a line from the centre, thus:

FIG. 1



An atom of carbon

FIG. 2



An atom of oxygen

FIG. 3

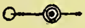
An atom of hydrogen

These forces are termed *valencies*, and the elements and their atoms are termed *monad*, *dyad*, *triad*, *tetrad*, &c., elements, according to the number of forces they are possessed of, and are said to be *mono-valent*, *di-valent*, *tri-valent*; &c., according to the number of valencies they have *free* to join other valencies.

As oxygen having two valencies will engage two of the four valencies of a carbon atom the other two can receive one other atom of oxygen, or in lieu of that two atoms of the monad hydrogen.

All these combinations would pictorially look thus:

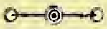
FIG. 4



One atom of oxygen with one of hydrogen

mono-valent

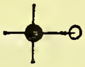
FIG. 5



One atom of oxygen with two of hydrogen

saturated

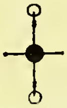
FIG. 6



One atom of carbon with one of hydrogen

tri-valent

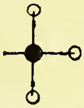
FIG. 7



One atom of carbon with two of hydrogen

di-valent

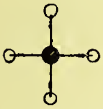
FIG. 8



One atom of carbon with three of hydrogen

mono-valent

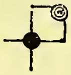
FIG. 9



One atom of carbon with four of hydrogen

saturated

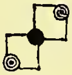
FIG. 10



One atom of carbon with one of oxygen

di-valent

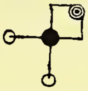
FIG. 11



One atom of carbon with two of oxygen

saturated

FIG. 12



One atom of carbon with one of oxygen and two of hydrogen

saturated

The free valencies have a strong craving for being saturated; so great is their need that they seize with avidity one of their own equals if they cannot get satisfied by anything better; in fact, the atoms are never, or with only a very few apparent exceptions (among the metals), found under ordinary circumstances to exist singly, and compounds of the organic world with any free valency are unknown.

A saturated atom or combination of atoms is, then, what we before defined as a *molecule*, that which could not be split up by mechanical means. In the above figures Nos. 5, 9, 11, and 12 are molecules, Nos. 5 and 11 composed of three, No. 12 of four, and No. 9 of five atoms.

The others are compounds with free valencies, and cannot exist in the free state; in their struggle for existence they combine mutually, or they split up and draw their supply from other molecules whose liberated valencies they then take possession of.

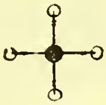
The atoms of the same element are all of equal size and weight, but differing from atoms of other elements. Their exact size and weight are not fully known, but the relation of weight between atoms of different elements is ascertained with considerable exactitude. Thus, for instance, we know that if a certain number of hydrogen-atoms weigh, say, one ounce, the same number of oxygen-atoms would weigh sixteen ounces; of carbon-atoms, twelve ounces, &c. These weight-relations are termed *atomic weight*. All atomic weights are different for different elements, varying from hydrogen's 1 to uranium's 239.

*Molecular weight* is the aggregate weight of all the atoms forming a molecule.

We are now prepared to approach our immediate object, to examine the structural building-up of all the individuals whose life and character make up the Organic Chemistry.

In all organic compounds carbon and hydrogen appear as never-failing constituents. From the simplest combination capable of existence, a carbon-atom with its four valencies bound to four atoms of hydrogen, all the rest of the organic world can gradually be built up. This compound is termed *methane*,

Fig. 13



Methane

and the first series derived from it are called Hydrocarbons.

# Part I.

# HYDROCARBONS

# Hydrocarbons

is the name given to this series on account of their constituents being hydrogen and carbon only. The growth of the organic world out of the simple molecule, methane, is effected by repeatedly removing one or more atoms of hydrogen, and placing some equivalent in lieu of them. The operation is called *substitution* or *replacement.* The way it is effected forms a convenient means for classification, which is necessary in order to save the immense number of organic individuals from hopeless confusion.

We divide them, therefore, first into two large sections, *hydrocarbons with open chains* and *hydrocarbons with closed chains.*

## HYDROCARBONS WITH OPEN CHAINS

Though everything organic may be considered as derived from methane these hydrocarbons have been specially termed methane derivatives on account of their more immediate origin from that molecule. Another and much older name is *the fatty group,* from the fact that many of its members occur in animal and vegetable fats; but, probably because this name does not sound sufficiently elegant, it has lately been transformed into the Greek version of the word 'fat,' and more refined and classically cultivated scientists would now say *the aliphatic series.*

The methane derivatives may be subdivided again by the position and number of hydrogen-atoms removed. The first of this series is

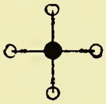
### Saturated or fundamental hydrocarbons

### Paraffins (with single bonds), $C_nH_{2n+2}$

NORMAL COMPOUNDS

No organic compound in which one or more valencies are left free can exist in the free state, as mentioned, p. 3. The simplest compound of carbon and hydrogen must therefore be one of the former and four of the latter, i.e. *methane.*

Fig. 14



One molecule of methane

One atom of carbon is also shortly written C, and one atom of hydrogen H; methane thus expressed would therefore be $CH_4$, which means a compound consisting of one atom of carbon and four of hydrogen.

Methane is a gas, and was originally named *marsh gas.*

What will now happen if we try to remove one of the atoms of hydrogen? It is not possible to experiment on one single molecule of methane; consequently we have not the slightest idea what would happen if we could. We must, as already mentioned, operate at least on millions or billions of molecules (although for obvious reasons they will hereafter be treated singly), and we can then succeed in removing one atom of hydrogen from each molecule. At the same moment that that is effected each molecule, having now a free valency, will seize on the free valency of its neighbour, and they will unite, forming a compound, *ethane*, in which all valencies are engaged, and consequently one capable of existence, i.e. a molecule. At the same time the two atoms of hydrogen removed, being also incapable of existence singly, will combine and form one *molecule* of hydrogen, illustrated thus:—

Fig. 15

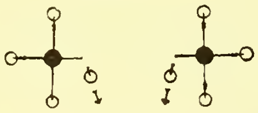


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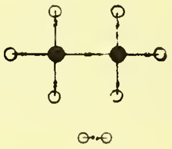
Fig. 16



Two molecules of methane = one molecule of ethane, $C_2H_6$, and one of hydrogen, $H_2$

If we now take another molecule of methane and a molecule of this new compound, ethane, and remove exactly in the same way one hydrogen-atom from each, the same process will take place as before.

Fig. 17

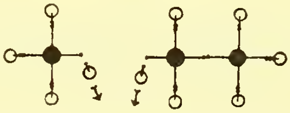


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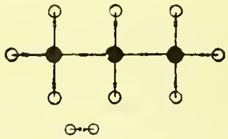
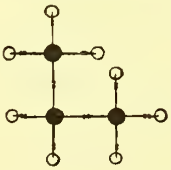
Fig. 18



One molecule of methane and one of ethane = one molecule of *propane*, $C_3H_8$, and one of hydrogen, $H_2$

We may perform the operation on any of the hydrogen-atoms of the end link, *e.g.*

Fig. 19



because it makes no difference so long as it is *the same* carbon-atom on which the different arrangements take place. It is the *succession* of the several carbon-atoms that is essential to the chemical character of the compound, and the succession is not altered in the above arrangements; it is only a bend which the chain makes round its intermediate carbon atom. Of course the individual links, as regards the kind and number of their appendices, must remain unaltered. For our purpose at present the rule holds good everywhere; generally our representations will be a straight chain, but in order the better to understand some processes it will be advantageous to make exceptions. Sometimes, dependent upon the character of the affixes to the carbon's valencies, such exceptions will prove to alter the physical properties of a compound, but we need not consider that here, as it will be fully gone through when we have to discuss atoms in space (p. 453).

Propane ($C_3H_8$) is a liquid below −17°, otherwise a gas.

Again, when we take a molecule of methane and one of propane ($C_3H_8$), the new compound, and repeat the process

FIG. 20

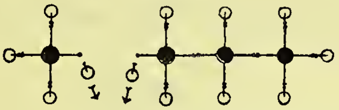
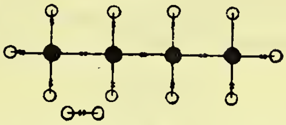


FIG. 21



One molecule of methane and one of propane = one molecule of *butane*, $C_4H_{10}$, and one of hydrogen, $H_2$

we then have another compound, butane ($C_4H_{10}$), a gas that condenses to a liquid at +1°.

We will once more take a molecule of methane and a molecule of the last compound, butane, and again remove two atoms of hydrogen.

FIG. 22

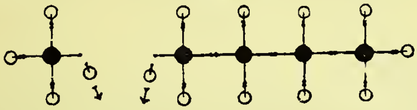
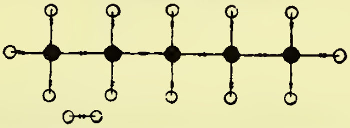


FIG. 23



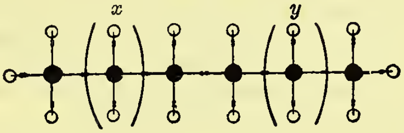
One molecule of methane and one of butane = one molecule of *pentane*, $C_5H_{12}$, and one of hydrogen, $H_2$

The new compound called pentane ($C_5H_{12}$) is a liquid at ordinary temperature, boiling at 37–39°, possessing an ethereal smell. Like all the foregoing compounds it is found in petroleum.

In the same way we can go on adding a molecule of methane to every new compound produced, removing at the same time a molecule of hydrogen.

For obvious reasons an abbreviated illustration of such heaping methane upon methane is a matter of necessity. In the figure below the arrangement will be understood without further explanation, except that 'x' and 'y' stand for any figure, including '0.'

FIG 24



As most of the fats have derivatives of the paraffins as constituents, some of them must be named:

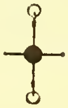
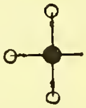
| | | | | | | |
|---|---|---|---|---|---|---|
| Normal hexane | (x + y = 2) | $C_6H_{14}$ | a fluid. | B. p. | 68°·5 | |
| ” heptane | (x + y = 3) | $C_7H_{16}$ | ” | ” | 98° | |
| ” octane | (x + y = 4) | $C_8H_{18}$ | ” | ” | 124° | |
| ” nonane | (x + y = 5) | $C_9H_{20}$ | ” | ” | 149°·5 | |
| ” decane | (x + y = 6) | $C_{10}H_{22}$ | ” | ” | 173° | |
| ” undecane | (x + y = 7) | $C_{11}H_{24}$ | ” | ” | 194°·5 | |
| ” dodecane | (x + y = 8) | $C_{12}H_{26}$ | ” | ” | 214°·5 | |
| ” tetradecane | (x + y = 10) | $C_{14}H_{30}$ | ” | ” | 252°·5 | |
| ” hedecane | (x + y = 12) | $C_{16}H_{34}$ | ” | ” | 287° | M. p. 18° |
| ” heptadecane | (x + y = 13) | $C_{17}H_{36}$ | ” | ” | 303° | ” 22°·5 |
| ” octadecane | (x + y = 14) | $C_{18}H_{38}$ | ” | ” | 317° | ” 28° |
| ” eicosane | (x + y = 16) | $C_{20}H_{42}$ | does not boil without decomp. | | | ” 36°·7 |
| ” docosane | (x + y = 18) | $C_{22}H_{46}$ | ” ” | ” | ” ” | ” 44°·4 |
| ” tetracosane | (x + y = 20) | $C_{24}H_{50}$ | ” ” | ” | ” ” | ” 51° |
| ” pentacosane | (x + y = 21) | $C_{25}H_{52}$ | not yet prepared | | | |

The highest hydrocarbon actually known is pentatriacontane ($C_{35}H_{72}$), but derivatives from a hydrocarbon as high as $C_{64}H_{130}$ are met with (theobromic acid, p. 178).

The nomenclature of these hydrocarbons from pentane is very simple and easy, being formed from the Greek ciphers.

It must be striking to anyone looking at the above figures how much they are like a chain consisting of a number of links of

FIG. 25 FIG. 26

$CH_2$ = , flanked at each end by a link of $CH_3$ = 

The theory by which organic chemistry has lately made such gigantic strides has therefore been named the *law of the linking of atoms*, and *chain* is quite an accepted word to designate the disposition of atoms in a molecule.

## RADICALS

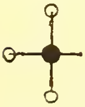
It will be noticed in the above examples that each compound may be looked upon as a joining of two kinds of links, one a methane from which one hydrogen-atom has been cut off (fig. 26), and the other either a methane from which two such atoms have been removed (fig. 25), or a chain with one hydrogen-atom removed (fig. 22). We will find as we go on that all compounds may be considered a joining of two other compounds, from each of which some part has been cut off, leaving one or more free valencies through which the rests of the compounds unite. Such rests are termed *radicals* (or synonymously *radicles*, *groups*, *residues*, *rests*). There are a great number of such remains of a molecule which we again and again meet with in different compounds, and which may be split off and, as it were, transplanted from one compound to another. On account of their frequent occurrence it has been found convenient to provide them with special names, as a rule systematically formed, though lack of agreement among chemists has unfortunately sometimes supplied more than one name to the same radical, or the same name to different radicals.

Radicals of paraffins may be looked upon as formed by splitting off one or more hydrogen-atoms from the hydrocarbons, and the nomenclature has been formed from the respective paraffin by changing the end syllable '*ane*' into '*yl*' when one hydrogen-atom has been removed, into '*ylidene*' when two, and into '*enyl*' when three such atoms have been split off.

The following table presents those most frequently used:

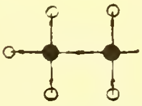
*Radicals formed by the removal of one hydrogen-atom, leaving one free valency (mono-valent radicals)*

FIG. 27



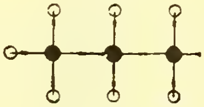
Methyl, $CH_3$

FIG. 28



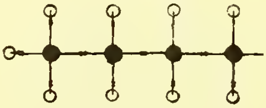
Ethyl, $C_2H_5$

FIG. 29



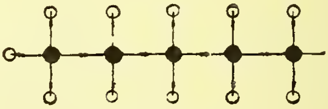
Propyl, $C_3H_7$

FIG. 30



Butyl, $C_4H_9$

FIG. 31

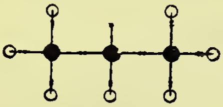


Pentyl or amyl, $C_5H_{11}$

Here the hydrogen-atom has been removed from the end-link: it is indifferent which of the three hydrogen-atoms connected with this last link of the chain be removed, as the valencies are of equal value.

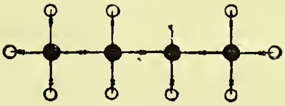
If the hydrogen is removed, not from one of the end-links, but from a link inside the chain, the radical is prefixed '*iso.*' Methane and ethane having no inside link, propane is the first to form an iso-radical:

Fig. 32



Iso-propyl, $C_3H_7$

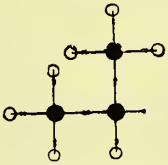
Fig. 33



Iso-butyl, $C_4H_9$

As mentioned, p. 8, the valencies being of equal value, it does not affect the chemical properties of a compound if the grouping round a carbon-atom is differently arranged, or, in other words, if the succession of the respective carbon-atoms remains the same; it is indifferent whether the chain represents a straight horizontal line or makes a bend at some particular point. Thus, instead of representing iso-propyl as above it may also be represented like this:

Fig 34



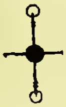
Iso-propyl, $C_3H_7$

Though the chemical properties are unaffected by such different grouping the physical properties may, as we have already mentioned, sometimes be affected; but, as a rule, we may say that it makes no difference.

(For further explanation and limitation of this rule see the stereometrical chemistry, p. 460.)

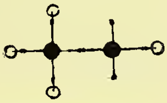
*Radicals formed by the removal of two hydrogen-atoms, leaving two free valencies (di-valent radicals):*

Fig. 35



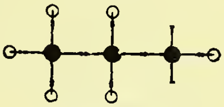
Methylidene or methylene, $CH_2$

Fig. 36



Ethylidene, $C_2H_4$

Fig. 37



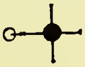
Propylidene, $C_3H_6$

Also here, any two hydrogen-atoms may be removed from the end-link without altering the chemical character of the radical. If two hydrogen-atoms are removed from *different* but *neighbouring* carbon-atoms, unsaturated hydrocarbons (p. 19) are formed, but if the carbon-atoms are *different* and *not neighbouring*, cyclo-compounds (p. 24) are formed.

*Radicals formed by the removal of three hydrogen-atoms, leaving three free valencies (tri-valent radicals):*

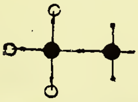
The only two to be mentioned here are

Fig. 38



Methenyl, CH

Fig. 39



Ethenyl, $C_2H_3$

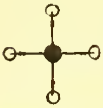
The others are radicals of unsaturated hydrocarbons, and will be found on p. 33.

It must be borne in mind that the use of radicals is solely a matter of convenience, and has nothing to do with the question of their actual existence, or non-existence, as isolated independent bodies.

## HOMOLOGOUS SERIES

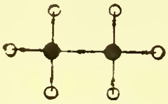
If we put those hydrocarbons we have just described, in a row, beginning with methane and ending with pentatriacontane ($C_{35}H_{72}$), abbreviated in the manner shown below for the sake of space

Fig. 40



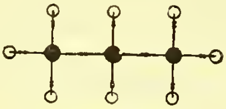
Methane, $CH_4$

Fig. 41



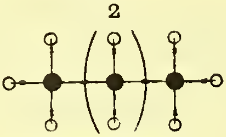
Ethane, $C_2H_6$

Fig. 42



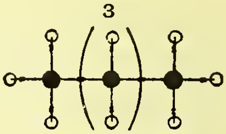
Propane, $C_3H_8$

Fig. 43



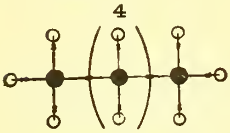
Butane, $C_4H_{10}$

Fig. 44



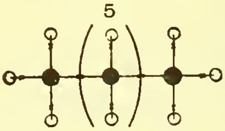
Pentane, $C_5H_{12}$

Fig. 45



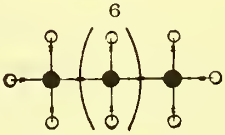
Hexane, $C_6H_{14}$

Fig. 46



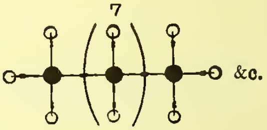
Heptane, $C_7H_{16}$

Fig. 47



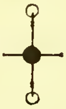
Octane, $C_8H_{18}$

Fig. 48



Nonane, $C_9H_{20}$

Fig. 49

we see there is a difference of one methylene  $=CH_2$ between every member of the series and its next neighbour. We shall hereafter become acquainted with more such series where the difference is $CH_2$ between the nearest members: they are termed *homologous series*, a characteristic of which is that all the members resemble each other closely in their chemical behaviour; their physical properties, however, undergo a gradual change proportionate to the increase in the number of carbon-atoms. Although often the extremities of a series may be widely different, two neighbours will be nearly identical.

Thus in the paraffin series the first four numbers are gases, methane having only recently been condensed to a fluid, whilst the fourth member, butane, is condensed by + 1°. The next members up to pentadecane ($C_{15}H_{32}$) are fluids at ordinary temperature with steadily rising melting and boiling points. The rest of the paraffins are solid, and boil without decomposition, only under diminished pressure, whilst the melting and boiling points still rise.

Shortly, homologous compounds may be described as chains formed in the same fashion, but from different numbers of methyl.

### ISOMERS

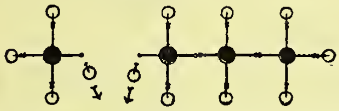
It will also have been noticed that all the compounds considered in the paraffin series were produced by substituting methyl for one of the atoms of hydrogen bound to the end-link of the chain. Now, it is indifferent (as already explained when discussing the radicals, p. 10) which of the hydrogen-atoms is replaced so long as it belongs to the same link; and for the sake of uniformity and better comparison we have preferred that the substitution take place on one of the extreme hydrogen-atoms of the chain. But the hydrogens of the end-links are not the only ones that may be replaced; a hydrogen-atom fixed to any of the intermediate links may just as well be displaced by methyl in a similar way. The products ensuing will have much the same chemical properties as the regular (normal) compound, but some of the physical characteristics, such as boiling and melting points, will show a difference. Such compounds are termed *isomers.*

We have described homologous compounds as chains formed in the same fashion but from different numbers of similar links; so we can say isomers are chains formed from the same number of similar links but in different fashion.[1]

It is evident that no isomers can be formed of any of the three first paraffins; the links cannot be placed in any other position that would make a difference in their mutual relations when we bear in mind the above rule about replacements on the same carbon-atom.

With *butane* the possibility of isomers commences. It will be remembered that the formation of butane (fig. 20, p. 9) is illustrated thus:

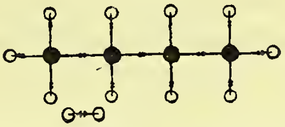
Fig. 50



One molecule of methane and one of propane

=

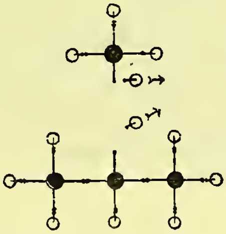
Fig. 51



= one molecule of butane, $C_4H_{10}$, and one of hydrogen, $H_2$

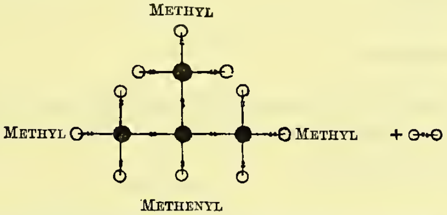
Methyl has replaced the extreme hydrogen-atom of propane; but if instead of this atom we remove one from the intermediate link, and place our methyl there,

Fig. 52



then we shall have a structure of this form:

Fig. 53



Isobutane, isopropyl-methane, or trimethyl-methane, $C_4H_{10}$

The new compound is a gas, colourless, condensable at a lower temperature by some degrees than butane, which, however, it otherwise closely resembles. When we look upon it from the central atom of carbon it appears like methane that has a methyl upon three of its four sides; hence the name of *tri-methyl-methane.*

---

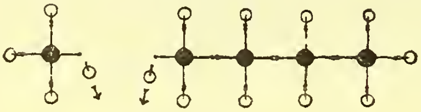
[1] The term 'isomerism' has been given widely different encompassments. Even if compounds have as little in common as have glycide alcohol (fig. 491, p. 116), hydroxy-propionic aldehyde (homologous to glycollic aldehyde, fig. 556, p. 135), propionic acid (fig. 669, p. 176), ethyl formate (fig. 862, p. 231), and methyl-acetate (fig. 863, p. 231), they are quite commonly spoken of as isomers, for the only reason that they happen to have the same empirical formula, $C_3H_6O_2$. As long as we did not understand upon what their differences were contingent, it might have been of speculative interest to comprise them in the term isomers, but with our present knowledge the interest is gone like that of a trick when we understand 'how it is done.'

Others have gone to the other extreme, and distinguished between *isomers*, *metamers*, and *isometamers*, divisions and subdivisions, with benefit to scarcely anybody but the printer.

We take the next member of the paraffin series, *pentane*, and see what can be done after the same fashion with that.

The formation of pentane was this (fig. 22, p. 9).

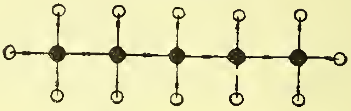
Fig. 54



Methane, $CH_4$ Butane. $C_4H_{10}$

=

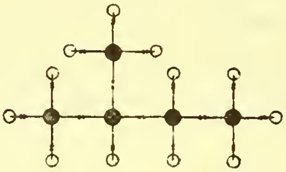
Fig. 55



Pentane, $C_5H_{12}$

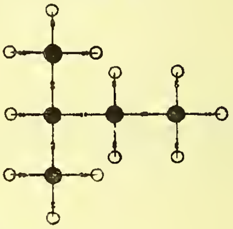
If we put methyl on one of the intermediate links we have

Fig. 56



or, if the methyl link to the left exchanges places with the hydrogen-atom on the same carbon-atom, which it can do, according to the rule, p. 8:

Fig. 57

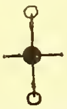


Di-methyl-ethyl-methane, pseudo-pentane, $C_5H_{12}$; b.p. 10°

We can look upon pseudo-pentane as methane which has had two of its atoms of hydrogen substituted by methyls, and the third by ethyl; hence the name.

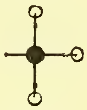
There is still a way, different from this, to arrange the links of carbon-groups. That part of the chain looking like ethyl is composed of

Fig. 58



Methylene

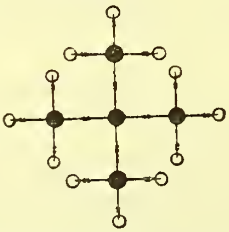
Fig. 59



Methyl

The latter will be recognised as a methyl-group, and can exchange places with the only atom of hydrogen left in the methane-group (fig. 56). When that is effected we have again a new compound:

Fig. 60



Tetra-methyl-methane: a fluid, b.p. 9°·5; above that temperature a gas

It is so named because, viewed from the central atom of carbon, it may be considered a methane in which all four atoms of hydrogen are substituted by methyl.

There are only these three different ways of arranging the four carbon-atoms with their atoms of hydrogen, when we remember that it is quite immaterial which of the atoms of hydrogen is removed and replaced by a methyl-group, as long as they belong to the same atom of carbon.

We will now give yet another example, and take for that purpose the next member of the paraffin series, *hexane.*

All hydrocarbons may be considered as composed of different numbers of methane from which have been removed atoms of hydrogen in pairs. Ethane is two molecules of methane less two atoms of hydrogen, or, what is the same thing, two methyl-groups. Propane is three molecules of methane less four atoms of hydrogen. Butane is propane and one methane less a pair of hydrogen-atoms; pentane is propane and two molecules of methane less two pairs of hydrogen-atoms; and finally hexane is propane with three molecules of methane less three molecules of hydrogen.

Fig. 61

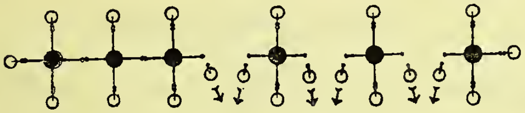


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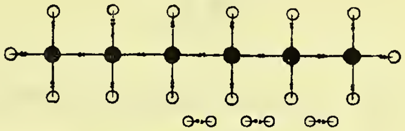
Fig. 62



Propane and three molecules of methane less three pairs of hydrogen atoms = one molecule of hexane + three molecules of hydrogen

As we have mentioned above there is only one way of arranging the carbon-atoms in propane; consequently the three carbon-groups must remain in the same position in all the variations we make with hexane. Three methane groups then remain which we can join to propane in any one of the four ways following, all differing from the above and from each other.

Of the three methane-groups we can place two at one end-link and the third at the other:

Fig. 63

1

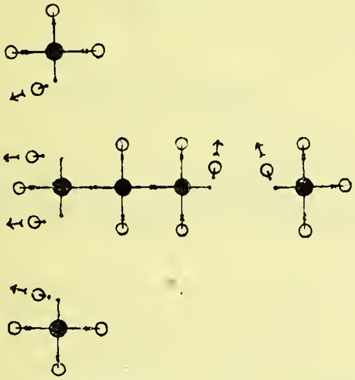


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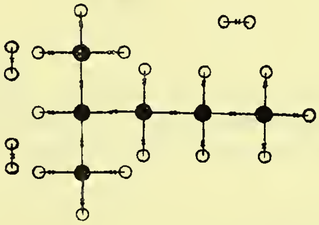
Fig. 64



Iso-hexane, di-methyl-propyl-methane, ethyl-isobutyl, $C_6H_{14}$; b.p. 62°

Or we can place a methane on each of the three links:

Fig. 65

2

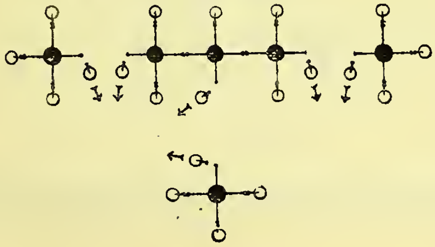


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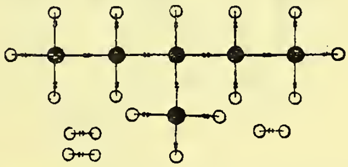
Fig. 66



Methyl-di-ethyl-methane, $C_6H_{14}$; b.p. 64°

Or two molecules of methane may be placed on one of the end-links, and the third on the centre-link.

FIG. 67

3

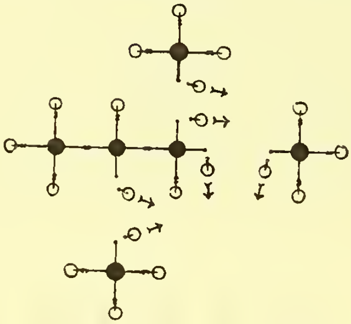


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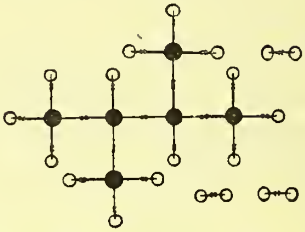
FIG. 68



Tetra-methyl-ethane, di-isopropyl, $C_6H_{14}$; b.p. 58°

Finally the three molecules of methane can substitute all three hydrogen-atoms on one of the end-links.

FIG. 69

4

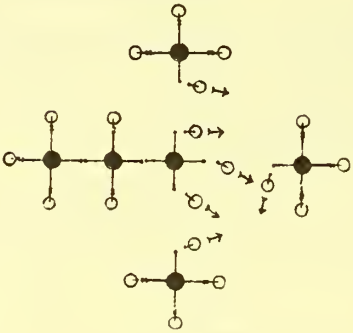


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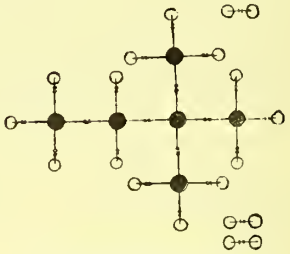
FIG. 70



Tri-methyl-ethyl-methane, $C_6H_{14}$; b.p. 43–48°

We have now five (including the original) different arrangements, and no more are possible. Any further attempt must produce one of the five results already shown; for instance, we have not yet placed two methyls on the central and the third on the end-link. We will try that also.

FIG. 71

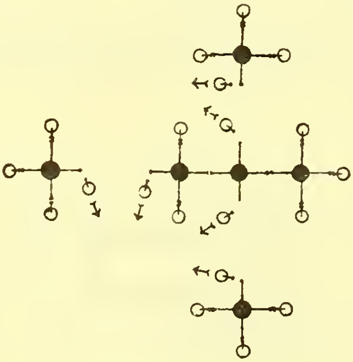


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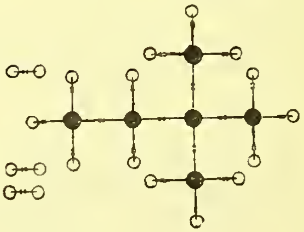
FIG. 72

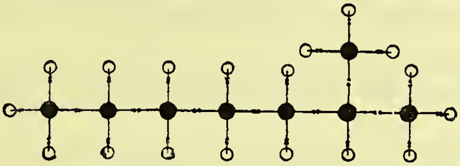


It will be seen at a glance that this arrangement is identical with that of tri-methyl-ethyl-methane, under No. 4, just above.

It remains only to make ourselves acquainted with some isomers from the rest of the paraffins, which we shall meet again more or less disguised.

From *octane*:

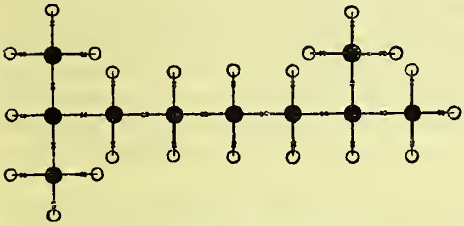
Fig. 73



Di-methyl-pentyl-methane, $C_8H_{18}$, hypothetical
Derivative: *m*-Xylene-hexa-hydride

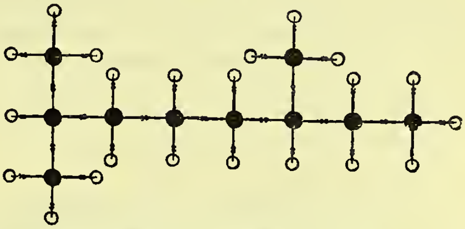
From *decane*:

Fig. 74



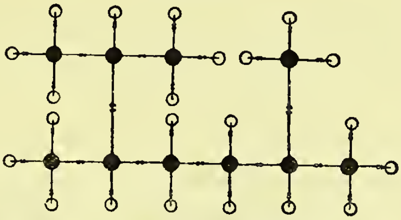
Di-methyl-iso-heptyl-methane,
di-iso-amyl, $C_{10}H_{22}$; b.p. 158°

Fig. 75



Methyl-ethyl-iso-hexyl-methane, $C_{10}H_{22}$
Derivatives: Cymene (fig. 142, p. 29); Geraniol (fig. 356, p. 74)

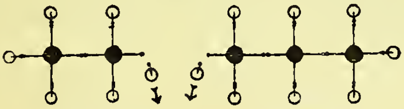
Fig. 76



Methyl-iso-propyl-pseudo-pentyl-methane, $C_{10}H_{22}$
Derivatives: Limonene (fig. 144, p. 29); Rhodinol (fig. 358, p. 74)

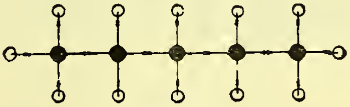
In order to show the gradual formation of the paraffins, we have built up the whole series by continually adding methane to every new compound formed, but of course we can make a short cut by joining two of the higher hydrocarbons. For instance, we have formed pentane by first joining two methanes, then adding successively three other methanes, always deducting two hydrogens, one from the compound lastly formed and one from the new methane; we can, however, also take an ethane and join it with a propane, and we obtain the same compound:

Fig. 77



=

Fig. 78



Ethane + Propane = Pentane

All the higher homologues as well as the isomers may be formed in this way from corresponding lower homologues of this series.

We have now had two forms of butane, three of pentane, and five of hexane. The several members of each class can scarcely be distinguished one from another in their chemical properties, the difference being often mainly in the boiling point and in their derivatives.

Such compounds of the same elements, in the exact proportion, and in similar quantities, with the like number of the same groups, but differing only in the arrangement of such groups, are termed *isomers*.

As already stated, methane, ethane, and propane can be arranged in but one way; in the hydrocarbons however, that now follow, the more numerous the carbon-atoms are, the more so are the isomers.

Butane has two isomers, pentane three, hexane five, heptane nine, octane eighteen, nonane thirty-five, decane seventy-five, and now it goes at an awful pace: 159, 357, 799, &c., according to the law of permutation; and when we come to the highest known hydrocarbon, pentatriacontane, $C_{35}H_{72}$, they might be counted by millions and billions.

This is theory; the fact is that save on paper the existence of not even fifty of all these millions is really established. The two butanes, three pentanes, and five hexanes are all prepared; but of the nine heptanes only five are known, of the eighteen octanes two, and a little higher up only one of each sort is known, and not always even that—in fact, the more numerous the isomers are expected to be, the fewer of them we find existing. This is remarkable: *pro primo*, it is lucky for those whose study is chemistry; *pro secundo*, it shows there must be a law of limitation somewhere of which we know nothing. But even fifty are a good number, and would form a quaint medley if not put into system.

When we look upon the illustrations of these hydrocarbons it must be obvious to the most casual observer that one of the classes looks like a single straight chain: these are the hydrocarbons first treated of, in which substitution always took place in the end-links. They are termed *normal paraffins*.

The other classes of hydrocarbons may be compared to a chain to which side-links are attached, and when substitutions take place in these side-links we forge as it were smaller branching chains on to the main one.

According to the mutual position of the carbon-atoms these hydrocarbons may be subdivided into three classes:

1. *Iso-paraffins*, in which not more than one of the carbon-atoms has three others attached (see 1 and 2, p. 15).
2. *Meso-paraffins*, in which two or more carbon-atoms are bound to three others (see 3, p. 16).
3. *Neo-paraffins*, in which one of the carbon-atoms is in direct connection with four others (see 4, p. 16).

From the paraffins, the class of compounds so far described, we can form different series of hydrocarbons by further abstraction of hydrogen-atoms in pairs.

According to the relative position of the carbon-atoms from which the hydrogen-atoms are removed these hydrocarbons may be divided into two large classes:

1. *Unsaturated hydrocarbons*, in which hydrogen-atoms are removed from neighbouring carbon-atoms.
2. *Cyclo-hydrocarbons*, in which hydrogen-atoms are removed from separated carbon-atoms.

Each of these two classes may be subdivided into several series, according to the number of hydrogen-atoms abstracted and the place which the carbon-atoms take up in the chain.

A short survey of their formation will first be given, followed by a specification to suit the purpose of this treatise

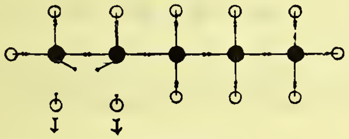
# FORMATION

## Unsaturated hydrocarbons

If we remove two hydrogen-atoms from two neighbouring carbon-atoms in any of the paraffin-compounds each of the latter will, of course, have a valency free; but, as mentioned before, free valencies cannot exist in any organic molecule, and the two thus liberated will have to join.

We can take as an example pentane:

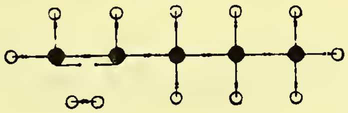
Fig. 79



Pentane

=

Fig. 80



Amylene

The two carbon-atoms are then said to be tied together by a *double bond*; but by this it must not be understood that the bond between them has become stronger than before; on the contrary, a double bond is always open to any offer, and willingly separates to receive and embrace disengaged hydrogen- or other monad-atoms, or even mono-valent groups, or radicals if their offer be more acceptable; nay, even more than that, the second bond seems to weaken the first so much that when a chain with such a double bond breaks the rupture will frequently take place just at the point where two carbon-atoms are so united.

The pictorial representation we have chosen for this state of linking is not meant to give a sketch of the process as it actually takes place. The doings of molecules and atoms can scarcely be understood from geometrical drawings if proper regard be had to their position in space. The perspective drawing of the simpler molecules is certainly within reach, and some will be subsequently given, but they need be very slightly complicated before it will be impossible to make out anything intelligible. If we can convey an idea of their several qualities and properties by geometrical drawings, we shall have achieved as much as one may reasonably expect.

Now, as to our representation of the double bond, it is intended to convey the idea of the altered character of the second bond; the ends of the two valencies being unable to touch each other, the binding cannot be as strong as that of the single bond. Further, the bristling of the valencies (mentioned p. 2) on the same carbon-atom should denote a certain antagonism between them, leaving them in their fullest vigour when at the greatest possible distance apart, but impairing the force by which they attract the valencies of other atoms when compelled to approach each other without full contact being effected.

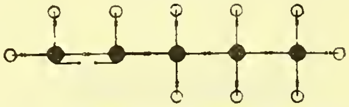
We now return to the further exposition of our hydrocarbons.

When we remove only two hydrogen-atoms from a paraffin-compound we get a series of hydrocarbons with one double bond, but otherwise exactly corresponding in structure to the paraffin series. This series is termed—

## The Olefines, or Ethylenes, $C_nH_{2n}$

They are normal when formed from a normal paraffin by abstracting the two hydrogen-atoms from the two extreme carbon-atoms at one of the ends of the chain; they are termed isomers if the double binding is effected between any other two carbon-atoms, or in any of the isomers of the paraffins, thus:

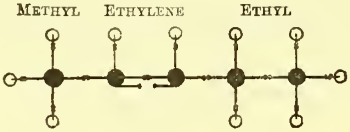
Fig. 81



Amylene, $C_5H_{10}$; b.p. 40°; from normal pentane (fig. 23, p. 9)

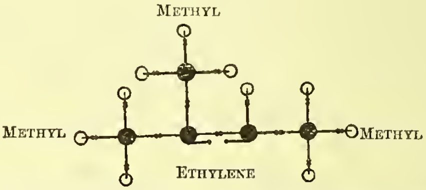
is a normal olefine, while the following are isomers:

Fig. 82



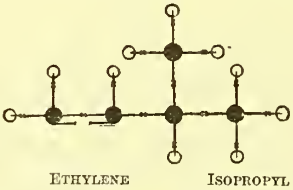
Methyl-ethyl-ethylene, $C_5H_{10}$; b.p. 36°; from normal pentane (fig. 23, p. 9)

Fig. 83



Tri-methyl-ethylene, pental, $C_5H_{10}$; b.p. 36–38°; from di-methyl-ethyl-methane (fig. 56, p. 14)

Fig. 84



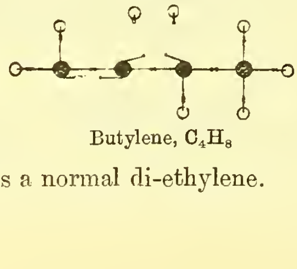
Iso-propyl-ethylene, $C_5H_{10}$; b.p. 21°·3; from di-methyl-ethyl-methane (fig. 56, p. 14)

## Di-ethylenes, $C_nH_{2n-2}$

We can again abstract two hydrogen-atoms from the olefines, and in one of two ways: either from the same two carbon-atoms from which we have already removed two atoms of hydrogen, or from some other pair of neighbouring carbon-atoms. By the first process we get the *acetylenes*, which will be described hereafter; by the second, the *di-ethylenes* are formed.

If we take away the two available hydrogen-atoms from the end of the chain most approximate to the existing double bond we obtain normal di-ethylenes; the removal of any others will result in isomers.

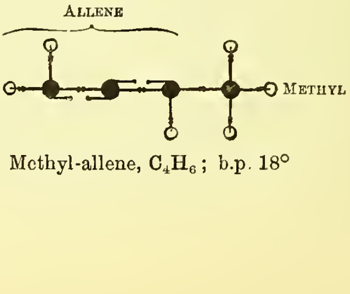
Fig. 85



Butylene, $C_4H_8$

=

Fig. 86

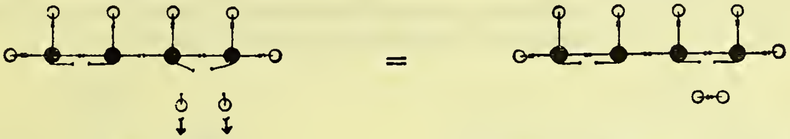


Methyl-allene, $C_4H_6$; b.p. 18°

Methyl-allene is a normal di-ethylene.

If we remove from the same compound two atoms of hydrogen from the other end of the chain we obtain the isomeric compound *butine*:

Fig. 87 Fig. 88

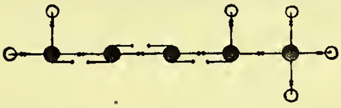


Butylene, $C_4H_8$ Butine (vinyl-ethylene), $C_4H_6$; b.p. 20°

## Tri-ethylenes, $C_nH_{2n-4}$

Again, two hydrogen-atoms may be abstracted from the di-ethylenes, in the same way as before. A normal hydrocarbon of this series would look like this,

Fig. 89



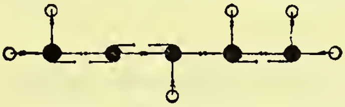
Methyl-tri-ethylene, $C_5H_6$

but is not known yet.

When the hydrogen-atoms are not all abstracted from the same end of the chain isomers are produced.

Such an isomer is *pirylene*, in which the abstraction is performed at the other end:

Fig. 90



Pirylene, $C_5H_6$; b.p. 60°

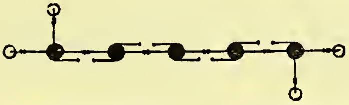
## Tetra-ethylenes, $C_nH_{2n-6}$

Lastly, two hydrocarbons may be removed from the tri-ethylenes as before.

Compounds with four double bonds were, however, entirely unknown until Heyerdahl discovered the therapic acid (fig. 770, p. 198), which is no doubt the most important constituent of cod-liver oil, both quantitatively and therapeutically.

A normal hydrocarbon of the tetra-ethylene series formed from methyl-tri-ethylene would have this structure:

Fig. 91



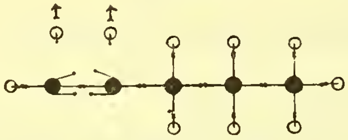
Tetra-ethylene, $C_5H_4$; hypothetical

Theoretically we might go on creating double bonds as long as we please, there being no limit but the length of the paper; practically, however, no more than four double bonds seem to exist. The chain appears unable to endure beyond a certain length, after which it breaks, as it were, by its own weight; the single binding being, however, more tenacious, a greater length of chain seems to be allowed to the paraffins.

## Acetylenes, $C_nH_{2n-2}$

Instead of removing the hydrogen-atoms from different pairs of neighbouring carbon-atoms in the compounds with double bonds, we may abstract them from the same two atoms that are already united by a double bond. We then obtain compounds with *triple bonds*, e.g.

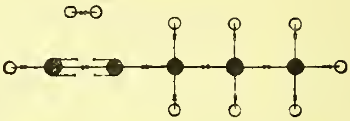
Fig. 92



Amylene, $C_5H_{10}$; b.p. 40°

=

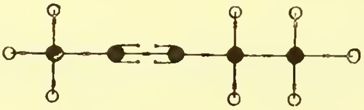
Fig. 93



Propyl-acetylene, $C_5H_8$; b.p. 48°

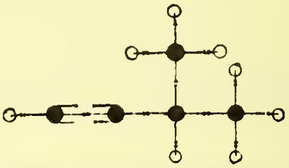
This is a normal acetylene for the same reasons that obtained with ethylene and poly-ethylene compounds (*vide* p. 20), whereas the following are isomers of the same compound:

Fig. 94



Valerylene, methyl-ethyl-acetylene, $C_5H_8$; b.p. 44°; from methyl-ethyl-ethylene (fig. 82, p. 20)

Fig. 95

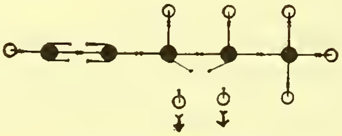


Iso-valerylene (iso-prene), $C_5H_8$; b.p. 28°; from iso-propyl-ethylene (fig. 84, p. 20)

## Di-acetylenes, $C_nH_{2n-6}$

From one of the homologues of acetylene, containing at least four carbon-atoms, we can abstract our usual two atoms of hydrogen. We will illustrate it by taking propyl-acetylene (fig. 93, above) as an example.

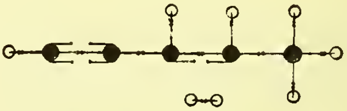
Fig. 96



Propyl-acetylene, $C_5H_8$

=

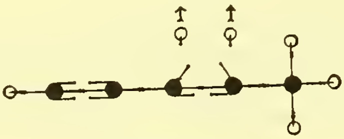
Fig. 97



Valylene, $C_5H_6$; b.p. 50°

This new compound, valylene, has a double and a triple bond, and forms an intermediate compound between acetylene and di-acetylene; removing two hydrogen-atoms from the doubly united carbon-atoms, di-acetylene is obtained.

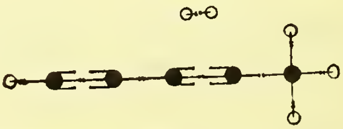
Fig. 98



Valylene, $C_5H_6$

=

Fig. 99

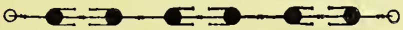


Methyl-di-acetylene, $C_5H_4$; hypothetical

## Tri- and tetra-acetylenes, $C_nH_{2n-10}$ and $C_nH_{2n-14}$

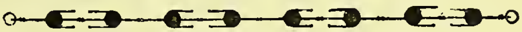
In the same way in which we have formed di-acetylenes from acetylenes, tri-acetylenes may be formed from di-acetylenes and tetra-acetylenes from tri-acetylenes. The process need not be reproduced; only a representation of these compounds will be necessary.

Fig. 100



Tri-acetylene, $C_6H_2$; hypothetical

Fig. 101

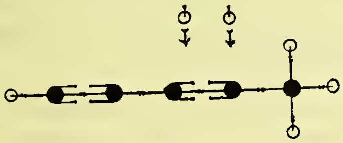


Tetra-acetylene, $C_8H_2$; hypothetical; for derivatives see Table IV. p. 174

Common to all hydrocarbons with double or triple bonds is, as mentioned p. 19, their ability to take up hydrogen or other monad atoms or mono-valent radicals until all the valencies are thus engaged. By this process the doubly or trebly linked compounds are at last turned into the corresponding paraffin-compounds when unable to take up any more atoms or radicals by simple addition. If we wish to add to the paraffins it can only be done by *substitution*, i.e. by exchange.

If we have, for instance, methyl-di-acetylene, it will first take up two hydrogen-atoms and become *valylene*.

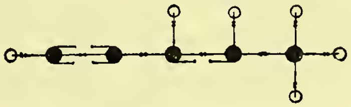
Fig. 102



Methyl-di-acetylene (fig. 99, p. 22)

=

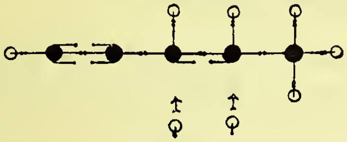
Fig. 103



Valylene (fig. 97, p. 22)

Adding another two hydrogen-atoms we have *propyl-acetylene*.

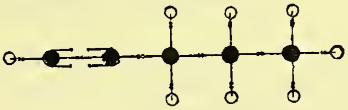
Fig. 104



Valylene

=

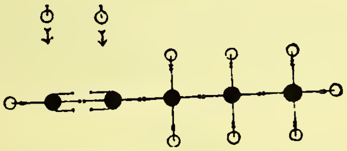
Fig. 105



Propyl-acetylene (fig. 93, p. 22)

Another two hydrogen-atoms produce *amylene*.

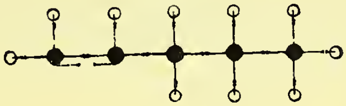
Fig. 106



Propyl-acetylene

=

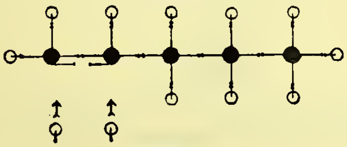
Fig. 107



Amylene (fig. 80, p. 19)

And lastly, the process repeated, we obtain *pentane*.

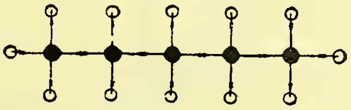
Fig. 108



Amylene

=

Fig. 109



Pentane (fig. 55, p. 14)

As will be seen this is the reverse process to forming the double and triple bonds. No more hydrogen-atoms can be added to pentane or any other paraffin; therefore they are termed *saturated hydrocarbons* (more fully referred to on p. 7 *et seq.*), and consequently all the others *unsaturated hydrocarbons.*

## CYCLO-HYDROCARBONS

### or Hydrocarbons with closed chains

We have, it will be remembered, formed all the preceding unsaturated hydrocarbons from the paraffins by abstracting hydrogen-atoms in pairs from two neighbouring carbon-atoms.

If the carbon-atoms from which we remove the hydrogen-atoms are not neighbours, the valencies set free must still join, as the compound cannot exist with free valencies; and they can only join in one way, that is, by the bending of the chain until the valencies meet, forming as it were a ring: hence the designation *cyclo* or *closed chains*, in contradistinction to the preceding hydrocarbons whose chains are termed *straight* or *open chains.*

Cyclo-hydrocarbons may be formed, not only from chains with single bonds (the paraffins), but also from chains with double bonds. Chains with triple bonds cannot form rings by the abstraction of hydrogen-atoms, but they can do so by a process termed polymerisation, changing their triple bonds into double ones. Accordingly the cyclo-hydrocarbons are divided into—

1. Compounds with single bonds only, and
2. Compounds containing double bonds. Each of these two classes is subdivided according to the number of links separating the two carbon-atoms deprived of their hydrogen-atoms.

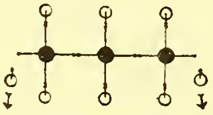
## Cyclo-hydrocarbons with single bonds, $C_nH_{2n}$

According to the number of intermediate carbon-atoms these hydrocarbons may be divided into five classes with one, two, three, four, or five intermediate links, all of them formed from the paraffin series. The first, termed

### Tri-methylene

is formed from propane

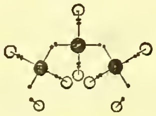
Fig. 110



Propane

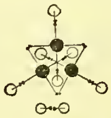
by abstracting a hydrogen-atom from each of the two carbon-atoms at the extremities, separated by the intermediate one.

Fig. 111



In the act of bending

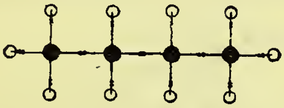
Fig. 112



The closed chain; tri-methylene, $C_3H_6$; a gas

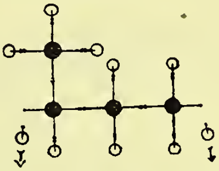
We may also abstract hydrogen-atoms in a similar position from longer chains, *e.g.* from butane.

Fig. 113



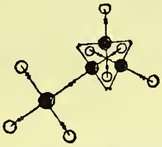
which may also be written (comp. p. 9)

Fig. 114



When we abstract the two hydrogen-atoms, as in fig. 110, we obtain this compound.

Fig. 115

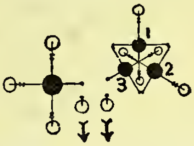


Methyl-tri-methylene, $C_4H_8$; hypothetical. Derivative: tri-methylene-carboxylic acid

The methyl is termed a *side-chain.*

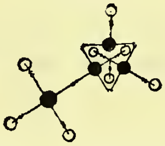
Nature forms the side-chains probably in this way; chemists in their laboratories form them mostly by substituting such radicals for one of the hydrogen-atoms in the closed chain.

Fig. 116



=

Fig. 117



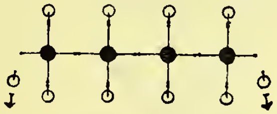
Methane + Trimethylene = Methyl-tri-methylene, $C_4H_8$

In order to distinguish between the different carbon-atoms in case of more than one side-chain being affixed, they are numbered as indicated above.

## Tetra-methylene

is the next compound where the two carbon-atoms from which hydrogen-atoms are to be removed are separated by two other carbon-atoms. It is formed from butane in the same way as tri-methylene from propane.

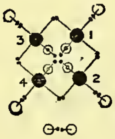
Fig. 118



Butane

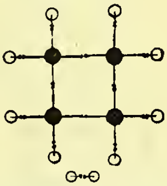
=

Fig. 119



or

Fig. 120



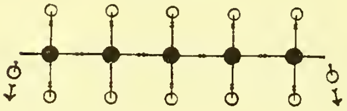
Tetra-methylene, $C_4H_8$

Tetra-methylene has not been isolated yet, but several derivatives are known (tetra-methylene carboxylic acids, p. 208), side-chains being formed in the same way as in tri-methylene.

## Penta-methylene

is formed by abstracting two hydrogen-atoms from two carbon-atoms separated by three other carbon atoms. It is formed from pentane as before.

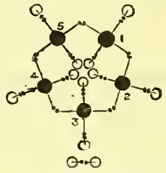
Fig. 121



Pentane, $C_5H_{12}$

=

Fig. 122

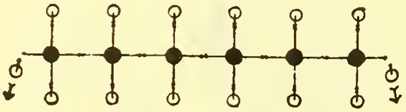


Pentaphane, penta-methylene, $C_5H_{10}$; b.p. 30°

## Hexa-methylene

is formed in the same manner from hexane, where four carbon-atoms separate the two.

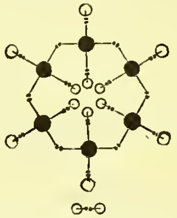
Fig. 123



Hexane, $C_6H_{14}$

=

Fig. 124

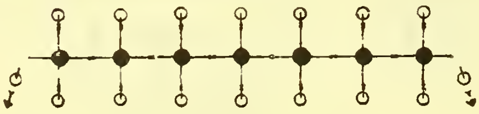


Hexa-methylene, benzene-hexa-hydride, $C_6H_{12}$; b.p. 69°; present with its homologues in Caucasian petroleum, and known by the collective name of naphthenes

## Hepta-methylene

It was long believed that no more than six carbon-atoms could form a ring, but three or four years ago a derivative of heptane was successfully turned into a ring (*Proc. Chem. Soc.* 1889, p. 145).

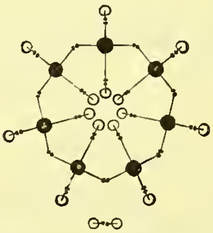
Fig. 125



Heptane, $C_7H_{16}$

=

Fig. 126



Hepta-methylene, $C_7H_{14}$

The hydrocarbon itself has not been prepared, but besides a homologue a few other derivatives have been obtained.

## Cyclo-hydrocarbons with double bonds

The double linkage in the open chain seems to give a certain stiffness to the chain, so much so that no ring appears capable of forming where three or more *neighbouring* carbon-atoms are united by double bonds as they are in all the normal poly-ethylenes.

When, however, the double bonds are separated by single unions, more elasticity comes into the chain, and if there be a sufficiency of links and of single bonds, the closing of the ring becomes possible.

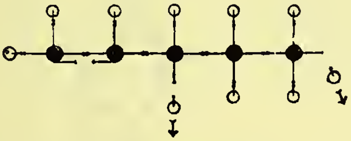
They may be classified by the sort of hydrocarbon from which they are formed; consequently we begin with the

### Olefine derivatives, $C_nH_{2n-2}$

There is, as we know, but one double binding in the olefines, but that is sufficient to exclude the possibility of closing a chain of three carbon-links. Whether four or five would be sufficient is doubtful; anyhow an independent ring is not known.

Of course a ring may be formed of amylene, which has five links, but then it would be a trimethylene with the double bond outside, not *in*, the ring.

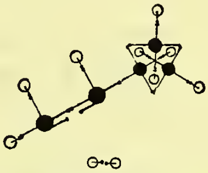
Fig. 127



Amylene

=

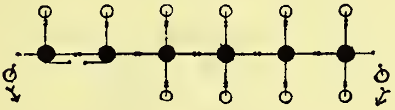
Fig. 128



Ethenyl-trimethyl, $C_5H_6$; hypothetical

From hexylene, however, a ring-shaped compound may be formed.

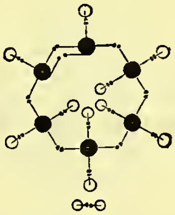
Fig. 129



Hexylene, $C_6H_{12}$

=

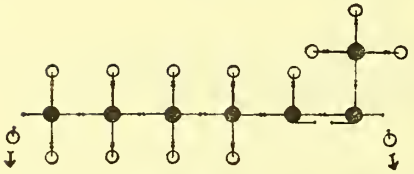
Fig. 130



Benzene-tetra-hydride, $C_6H_{10}$

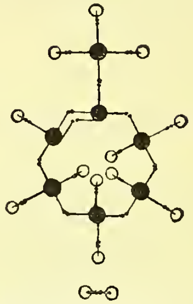
A closed chain consisting of more than six links and formed from an olefine is not known. Any link beyond the six will form side-chains (*vide* p. 25); for instance:

Fig. 131



β-Heptylene, $C_7H_{14}$; b.p. 98° (*vide* fig. 193, p. 36)

Fig. 132

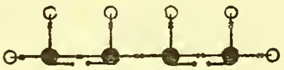


Toluene-tetra-hydride, $C_7H_{12}$; b.p. 103–105°

## Di-ethylene derivatives, $C_nH_{2n-4}$

The first di-ethylene with a single bond between the two double bindings is butine (*vide* fig. 88, p. 21),

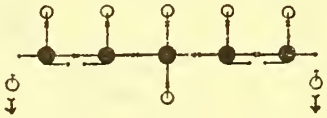
Fig. 133



Butine, $C_4H_6$

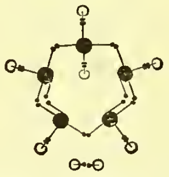
but it is not flexible enough to be bent into a closed ring; it is only when another link is interpolated that a perfect ring can be formed.

Fig. 134



Piperylene, $C_5H_8$; b.p. 42°
(fig. 200, p. 38)

Fig. 135

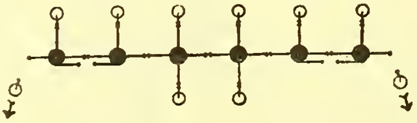


Cyclo-pentadiene or pentaphene, $C_5H_6$ (Congress nomenclature); hypothetical

An independent ring is not known, but in a few more complex compounds a structure of this form is supposed (*e.g.* fluoranthene, indene, *Ber.* xxiii. p. 3276).

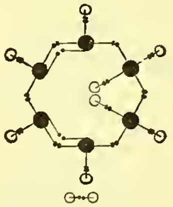
When a sixth link is added or interposed an independent ring can easily be formed.

Fig. 136



Di-allyl, $C_6H_{10}$; b.p 59° (*vide* fig. 201, p. 38)

Fig. 137



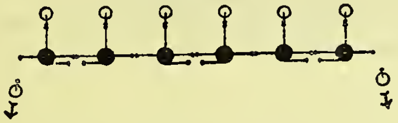
Benzene-dihydride, $C_6H_8$; b.p. 80° (*Ber.* xxv. p. 1840)

More than six carbon-atoms in a ring with double bonds are unknown. Any extras would go to form side-chains as before explained.

## Tri-ethylene derivatives, $C_nH_{2n-6}$

Double bonds are incapable of bending unless they are separated by at least one single bond, and these rings cannot be formed of more than six carbon-atoms; therefore the only hydrocarbon fulfilling the conditions is a hexone of this structure.

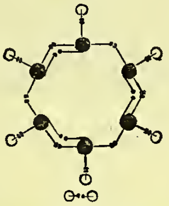
Fig. 138



Hexone, $C_6H_8$ (*vide* p. 41)

=

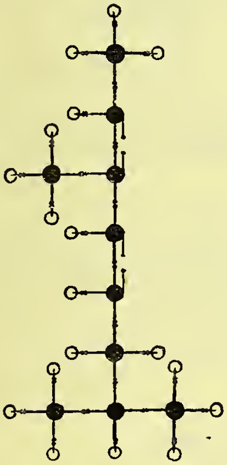
Fig. 139



Benzene, $C_6H_6$; b.p. 80°·5

If an open chain, capable of being formed into a benzene-ring, has side-chains, these will remain as such on the benzene.

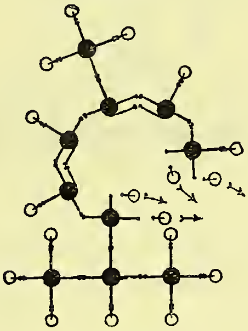
Fig. 140



Di-methyl-butinyl-iso-propyl-methane

=

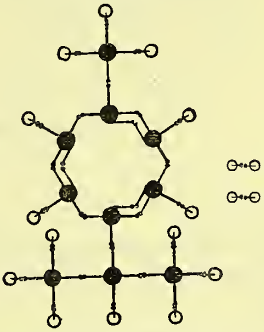
Fig. 141



Closing

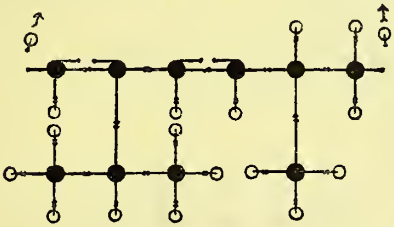
=

Fig. 142



Methyl-iso-propyl-benzene (cymene), $C_{10}H_{14}$; b.p. 175°; a constituent of Roman cumin oil; has been prepared from geranial, the aldehyde derived from di-methyl-butinyl-iso-propyl-methane (*vide* fig. 553, p. 133; *Ber.* xxiv. p. 205)

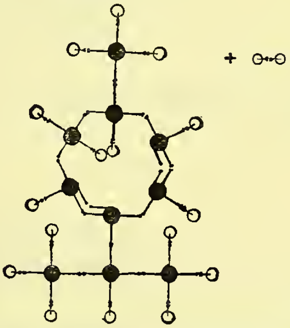
Fig. 143



Di-iso-propyl-butine

=

Fig. 144



Methyl-iso-propyl-benzene-di-hydride (limonene?), $C_{10}H_{16}$; b.p. 175°

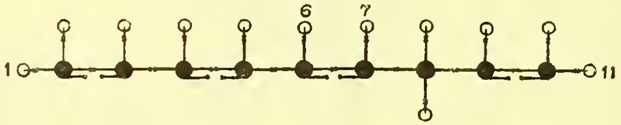
Cymene and limonene are natural products, constituents of many ethereal oils, and, again, this is probably the way in which nature forms these rings from open chains, as mentioned p. 25, whilst chemists in most cases take a more or less complex benzene compound on which by various processes radicals are hooked on, split off, or exchanged. Both because the formation of rings from open chains, specially the more complex ones, is known for comparatively few compounds, and because it is much easier to compare and classify the enormous number of compounds belonging to this class when looked upon as formed by substitution, abstraction, or addition, we also shall, as a rule, regard them as formed in this way. Thus the above two compounds are, as the names indicate, one a benzene ring, the other a benzene di-hydride, in each of which two of the hydrogen-atoms are substituted, one by a methyl-, the other by an iso-propyl-radical.

## Poly-ethylene derivatives

No more than six carbon-atoms in a doubly linked open chain without side-chains can form one ring, but if there is a sufficient number the chain will make another bend, and two or more—as it were—interlocked rings may be formed, and are termed *condensed nuclei*.

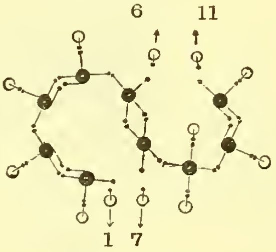
Suppose, for instance, we have a chain of nine atoms of carbon linked together in this fashion;

Fig. 145



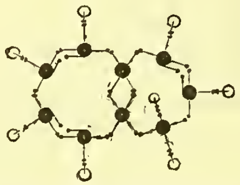
and the hydrogen-atoms marked 1, 6, 7, and 11 are removed; the straight chain will bend serpent-like, and finally shut up, forming two interlocked rings: one, a benzene ring, the other a pentaphene ring.

Fig. 146



=

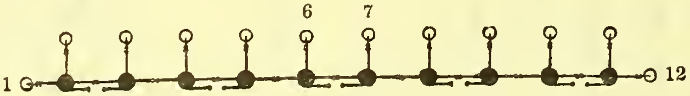
Fig. 147



Indene, $C_9H_8$; b.p. 180° (*Ber.* xxiii. p. 3276)

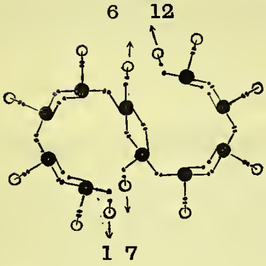
Another instance. Suppose we have a chain of ten carbon-atoms like this

Fig. 148



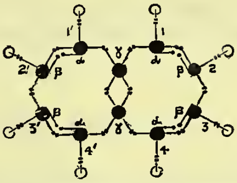
and the hydrogen-atoms 1, 6, 7, and 12 are removed, the bending and closing will appear thus:

Fig. 149



=

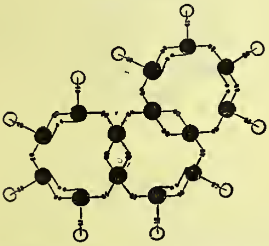
Fig. 150



Naphthalene, $C_{10}H_8$; m.p. 80°; used in the preparation of various dyes, and for the carburation of illuminating gas

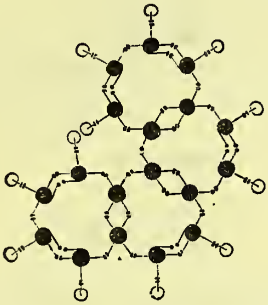
Further, an open chain of fourteen, eighteen, or twenty-two carbon-atoms would form three, four, or five rings of the same sort.

Fig. 151



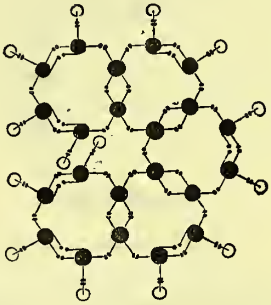
Phenantrene, $C_{14}H_{10}$; m.p. 100°

Fig. 152



Chrysene, $C_{18}H_{12}$; m.p. 248°

Fig. 153

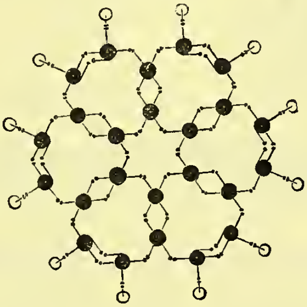


Picene, $C_{22}H_{14}$; m.p. 364° (*Ber*. xxvi. p. 1751)

Picene boils at 520°, i.e. nearly at red heat, and has therefore the highest boiling-point of any known hydrocarbon (*R. & S.* VI. p. 552).

It is the final member of this series, but theoretically there is room for another ring before the circle is closed.

Fig. 154



$C_{24}H_{12}$

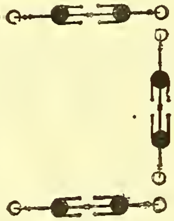
It is not found yet, but once found it is sure to beat picene in the point of both melting and boiling.

Open chains with double bindings of such length as these ring-formations would require are certainly unknown, but, for all we know to the contrary, they may be momentarily formed preceding the formation of the ultimate compound. Or the ring may be welded from smaller chains which taken together would make up the more lengthy one, just as we are now going to see the same compounds formed from several pieces of acetylene.

## Derivatives from hydrocarbons with triple bonds

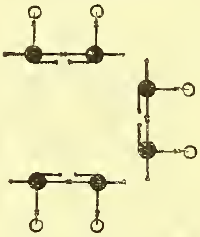
The triple bond imparts a still greater rigidity to the open chain; even when alternating with single bonds no closure of the ring has hitherto been effected; still the benzene-ring can be formed from acetylene, but only by three separate molecules being welded together, a process termed *polymerisation.* In this case the triple bonds break, double bonds being formed. The process is represented in this way:

Fig. 155



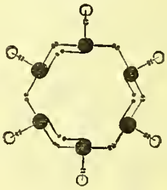
Three molecules of acetylene

Fig. 156



The triple bonds broken

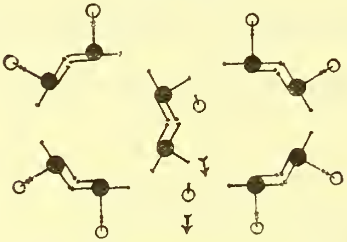
Fig. 157



Benzene formed

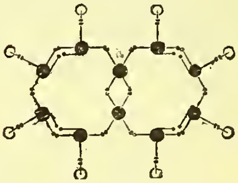
From five acetylenes we obtain, by abstracting two hydrogen atoms, *naphthalene.*

Fig. 158



Five molecules of acetylene

Fig. 159



Naphthalene

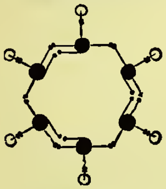
By the same process we can form phenantrene from seven molecules, chrysene from nine, and picene from eleven molecules of acetylene.

### GENERAL REMARKS ON THE RING-FORMED COMPOUNDS

The closing of the chain alters to a great extent the properties of the compound. It becomes very stable, and the ring is not easily broken. Whereas *additions* to straight chains with double bonds are easily effected, it is difficult to break the double bond in the ring-shaped compounds, very energetic reactions being required for this purpose. In our pictorial representation this fact is illustrated by the double bonds being brought into contact with one another through the bending, and thus *tied* together much more strongly than in the straight chain, where they are only *approaching* each other.

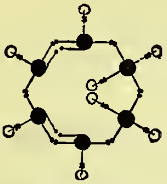
Still, additions (*hydration*) are possible first of two, then of four, and lastly of six hydrogen-atoms.

Fig. 160



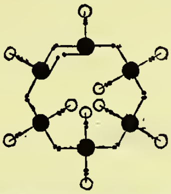
Benzene, $C_6H_6$; b.p. 80°·5

Fig. 161



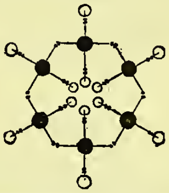
Benzene-di-hydride, $C_6H_8$; b.p. about 80° (*Ber.* xxv. p. 1840)

Fig. 162



Benzene-tetra-hydride, $C_6H_{10}$; b.p. 82° (*Ber.* xxvi. p. 230)

Fig. 163



Benzene-hexa-hydride, $C_6H_{12}$; b.p. 69°

These are the identical compounds we have already formed from open chains (*vide* figs. 137, p. 28, and 130, p. 27; fig. 124, p. 26), and they are termed *hydrated* benzenes.

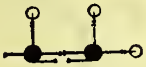
In return, these added hydrogen-atoms are again easily removed; those outside the ring are much more readily exchanged against many radicals than those of open chains. Generally, the open chains with double bonds are more capable of *additions* than of substitutions, the closed chains accepting *substitutions* more readily than additions.

## RADICALS

We have already (p. 10) given a definition of what is understood by radicals, and specified those from the paraffin series commonly made use of. As we frequently meet with similar groups formed from the other hydrocarbons, an enumeration of these, too, is rather necessary in order to properly understand the language of chemistry.

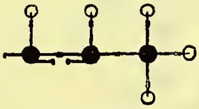
From *olefines* are derived—

Fig. 164



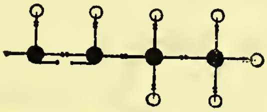
Vinyl, $C_2H_3$

Fig. 165



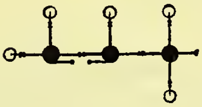
Propenyl, $C_3H_5$

Fig. 166



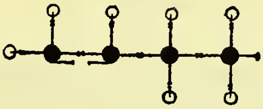
Crotonyl or Butenyl, $C_4H_7$

Fig. 167



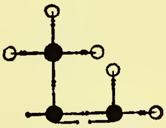
Allyl, $C_3H_5$

Fig. 168



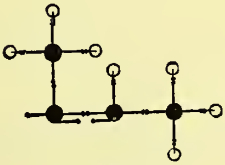
Butylenyl, $C_4H_7$

Fig. 169



Iso-propenyl, $C_3H_5$

Fig. 170

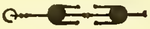


Iso-crotonyl, $C_4H_7$

Authors are not always careful how they use the nomenclature; *vinyl* is by some termed *ethenyl* (*vide* fig. 39, p. 11), *allyl* being occasionally applied to *propenyl*, sometimes termed *iso-allyl*; in return *propenyl* becomes *allyl*, and *iso-propenyl*, *propenyl*. The above names are, I think, those most in use.

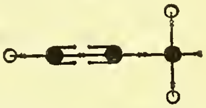
From *acetylene* are derived—

Fig. 171



Acetenyl, $C_2H$

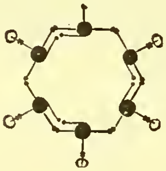
Fig. 172



Propinyl or propargyl, $C_3H_3$

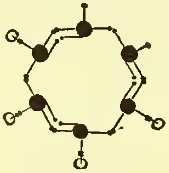
From *benzene* are derived—

Fig. 173



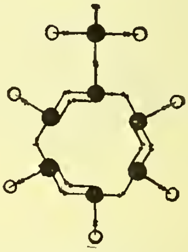
Phenyl, $C_6H_5$

Fig. 174



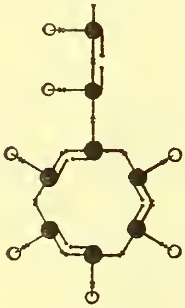
Phenylene, $C_6H_4$

Fig. 175



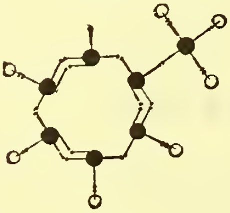
Benzyl, $C_7H_7$

Fig. 176



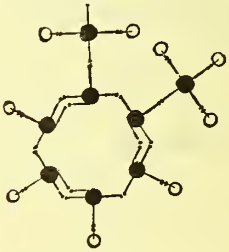
Cinnamenyl, $C_8H_7$

Fig. 177



Tolyl, $C_7H_7$

Fig. 178



Tolyl, Xylyl, $C_8H_9$

Some chemists use the term *tolyl* for the second of these structures, some for the third; no agreement has been come to as yet, though there has been no want of proposals. The above figures represent the ortho-radicals, but there are, of course, also meta- and para-tolyls (*vide* p. 43).

# SPECIFICATION

Having now made ourselves acquainted with the general mode of formation of the different series of unsaturated and cyclo-hydrocarbons derived from the paraffins, we may consider more in detail those of them that have a special interest either to medical science or to the further development of our treatise. We discuss them in the same order of evolution as on the preceding pages.

## Olefines, $C_nH_{2n}$

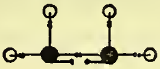
### NORMAL

The whole series of normal olefines, up to those comprising molecules with sixteen carbon-atoms, are known. Of the still higher homologues those only with eighteen, twenty, twenty-seven, and thirty, and derivatives of the one with twenty-two carbon-atoms, are known to exist, or to have been prepared.

The nomenclature of the olefines has been formed by adding the suffix '*ene*' to the end syllable '*yl*' of the mono-valent radicals of the paraffins, ethyl, ethylene; propyl, propylene, pentyl, pentylene, &c., or the syllable '*yl*' is changed into '*ene*.'

The first member of this series is ethylene:

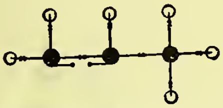
Fig. 179



Ethylene (ethene), $C_2H_4$

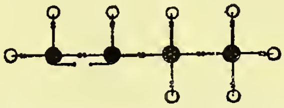
Then follow:

Fig. 180



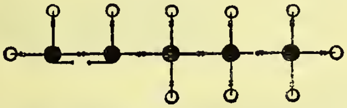
Propylene (propene), $C_3H_6$; a gas

Fig. 181



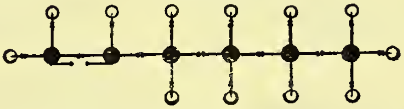
Butylene (butene), $C_4H_8$; a gas

Fig. 182

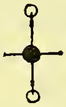


Amylene, pentylene (pentene), $C_5H_{10}$; b.p. 40°

Fig. 183



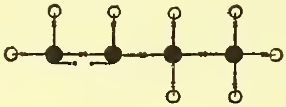
Hexylene, $C_6H_{12}$; b.p. not ascertained

further, heptylene, $C_7H_{14}$, and so on, constantly adding a methylene  (*vide* p. 9) for every new homologue. The lowest members are gases gradually passing into liquids, the boiling-point rising with the number of carbon-atoms; the higher members, i.e. from twelve carbon-atoms, are solids with a rising melting-point. In their physical properties they resemble the paraffins closely.

### ISOMERS

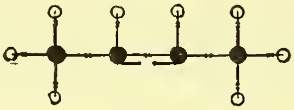
The first olefine from which we can expect to find isomers is butylene, $C_4H_8$. Three are not only possible, but also known.

Fig. 184



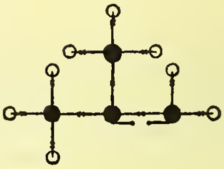
Normal or α-butylene, $C_4H_8$

Fig. 185



Pseudo- or β-butylene, $C_4H_8$

Fig. 186



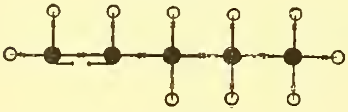
Iso-butylene, $C_4H_8$

all three gaseous, with boiling-points between −6° and +1°.

In order to indicate by the names the position of the various carbon-atoms in straight chains a proposal (*Ber.* xix. p. 160) has been generally adopted for marking the end carbon-atoms ω and ω′, and the others in succession α, β, &c., from one end, and α′, β′, &c., from the other. The letters of the Greek alphabet also betoken the position of any special bond, beginning from the end with α.

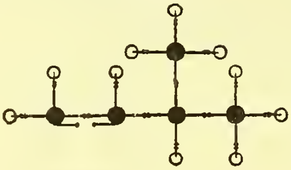
The five links of the next olefine, amylene or pentylene, $C_5H_{10}$, may be put together in five different arrangements, and are all actually known.

Fig. 187



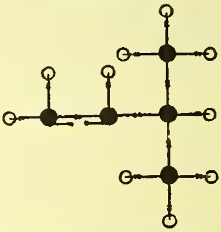
Normal amylene, propyl ethylene, $C_5H_{10}$; b.p. 39°

Fig. 188



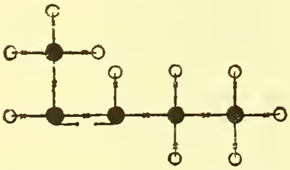
or

Fig. 189



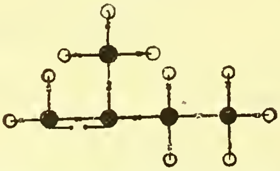
Iso-propyl ethylene, $C_5H_{10}$; b.p. 21°; is present in turpentine

Fig. 190



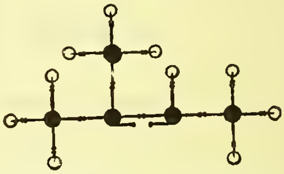
α-Methyl-ethyl-ethylene, $C_5H_{10}$ b.p. 36°

Fig. 191



β-Methyl-ethyl-ethylene, $C_5H_{10}$; b.p. 36°

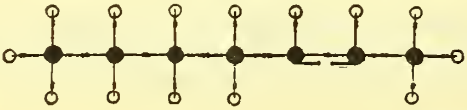
Fig. 192



Tri-methyl-ethylene, β-iso-amylene, pental, $C_5H_{10}$; b.p. 36°; an anæsthetic, mustard-like smell

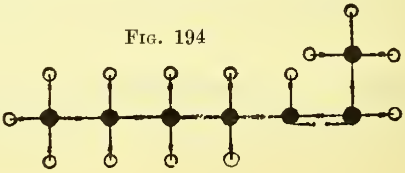
Commercial amylene is a mixture of pentanes and pentenes (pentylenes) containing chiefly tri-methyl-ethylene, which, in a chemically pure state, has recently been introduced as an anæsthetic in dental surgery under the name of pental; but its use has already been attended with unpleasant and even dangerous by-effects (*Therap. Monatssch.* 1893, p. 44; *Ph. C.* xxxiv. pp. 51, 271), three fatalities in 593 narcoses (*D. med. Zeit.* 1893, p. 364).

Fig. 193



or

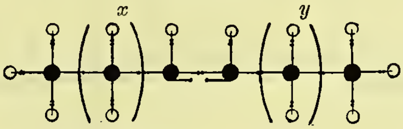
Fig. 194



β-Heptylene, $C_7H_{14}$; b.p. 98°

Amongst the higher olefines the isomers that have been prepared are but few, and their structures mostly unascertained, although some of their derivatives are of the greatest interest in the study of oils and fats. Their structures may be illustrated thus:

Fig. 195



'$x$' and '$y$' stand for any cipher, including '0.'

The following, though only known through their derivatives, need special mention:

| | |
|---|---|
| An isomer of Hendecylene | $C_{11}H_{22}$ $(x+y=7)$ |
| " " " Hexadecylene | $C_{16}H_{32}$ $(x+y=12)$ |
| " " " Octadecylene | $C_{18}H_{36}$ $(x+y=14)$ |
| " " " Nonadecylene | $C_{19}H_{38}$ $(x+y=15)$ |
| " " " Docosylene | $C_{22}H_{44}$ $(x=18, y=0)$ |

All the normal paraffins are found in nature chiefly in petroleum wells, from which the gaseous hydrocarbons are evolved as soon as the pressure ceases that holds them in solution in the crude oil. Thus the holy fire at Baku, which has been burning as long as history goes back, and fire-damp in coal-pits, are methane or marsh gas. From some oil-wells in America, methane, ethane, propane, but chiefly butane, issue and are conducted through pipes, and utilised for lighting and other technical purposes. These gases are also condensed by pressure and employed in the preparation of ice under the name of *cymogene.* After the gases have escaped from the petroleum oil the rest, consisting of fluid and solid hydrocarbons, is distilled, and that which is collected under 18° is known as *rhigolene*, and used as an anæsthetic. That which is boiling below 60–80° is a mixture of pentane and hexane, and bears the name of *petroleum-ether* or *naphtha*, and with a still higher boiling-point, 80–120°, is termed *gasolin, benzin, ligroin* (a mixture of heptane and octane). At the rise of boiling-point to 120–160° we have *artificial turpentine*, and going yet higher to 170–300° are the hydrocarbons $C_{10}$ to $C_{20}$ recognised as *standard kerosene*, *mineral sperm oil*, &c. Above this (b.p. 300°) are chiefly the solid hydrocarbons ($C_{21}$–$C_{27}$), from which are obtained *vaselin* and lubricating oils.

The Russian petroleum differs from the American in containing hydrated cyclo-hydrocarbons, $C_nH_{2n}$ (*vide* fig. 124, p. 26), and olefines. They do not give any vaselin, but only lubricating oils, which, either alone or mixed with *ozokerit*, form the *unguentum paraffini* of the Pharmacopœias.

*Ozokerit* is a mixture of pure solid paraffins prepared from a natural product found in Galicia and the Caucasus; besides which Texas, Arizona, and Utah are said to be rich in such deposits.

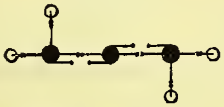
By the distillation of brown-coal, bituminous shale, boghead cannel, lignite, or peat a variety of substances containing paraffin hydrocarbons are obtained. *Naphtha*, with the lowest boiling-point; *photogen*, between 100° and 140°; *kerosene, paraffin oil*, and *solar oil*, from 200–300°. Over 300° distils the solid *paraffin* used for candle making. A great proportion of *paraffin* is now prepared also from American crude petroleum.

## Di-ethylenes, $C_nH_{n-2}$

### NORMAL

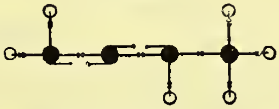
There are only two normal di-ethylenes as yet known.

Fig. 196



Allene, iso-allylene, $C_3H_4$; a gas

Fig. 197

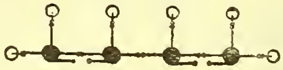


Methyl-allene, $C_4H_6$; b.p. 18°

### ISOMERS

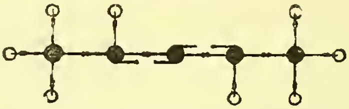
The isomers themselves are of little importance, but some of their derivatives, as we subsequently shall see, are constituents of some well-known fats. As examples of this class may be mentioned—

FIG. 198



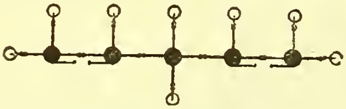
Vinyl-ethylene, butine, $C_4H_6$; b.p. 20°

FIG. 199



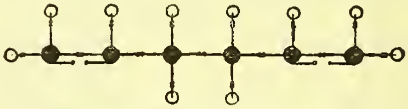
Di-methyl-allene, $C_5H_8$; b.p. 30–40°

FIG. 200



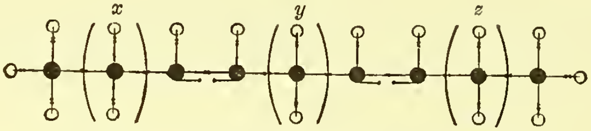
Piperylene, $C_5H_8$; b.p. 42°

FIG. 201



Di-allyl, hexine, $C_6H_{10}$; b.p. 59°

FIG. 202



An isomer of octadecatylidene, $C_{18}H_{34}$ $(x+y+z=12)$

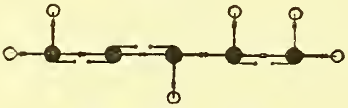
## Tri-ethylenes, $C_nH_{2n-4}$

No normal compound of this class is known.

### ISOMERS

Only a few of recent date have been prepared, *e.g.*

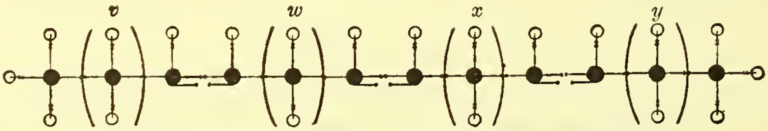
FIG. 203



Pirylene, $C_5H_6$; b.p. 60°

and derivatives from two others (*linolenic* and *iso-linolenic acid*) are recognised.

FIG. 204



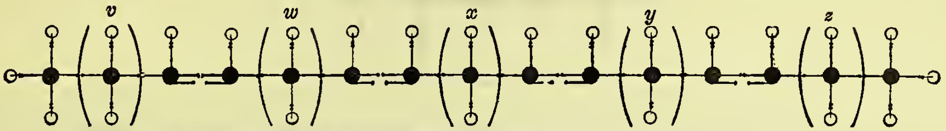
Isomers of octa-deca-tri-ethylene, $C_{18}H_{32}$ $(v+w+x+y=10)$

## Tetra-ethylenes, $C_nH_{2n-6}$

No hydrocarbon of this class nor any derivatives were known before the discovery of *therapic acid* in cod-liver oil (fig. 770, p. 198).

The structure of the hydrocarbon from which this remarkable acid is derived may be represented thus:

Fig. 205



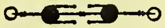
Isomer of hepta-deca-tetra-ethylene, $C_{17}H_{28}$ ($v+w+x+y+z=7$)

## Acetylenes, $C_nH_{2n-2}$

### NORMAL

The first member of this class is *acetylene*.

Fig. 206

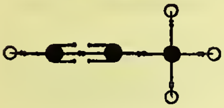


Acetylene, $C_2H_2$; a gas

Acetylene possesses an unpleasant smell, and is always present in coal gas, which owes its peculiar odour mainly to this compound. It is most interesting on account of its direct formation from carbon and hydrogen when an electric arc passes between two carbon poles in an atmosphere of hydrogen. The two elements are here, without the agency of organic life, united and formed into a molecule from which the whole organic world may be built up. Curiously enough, the electric spark will again decompose it into its elements.

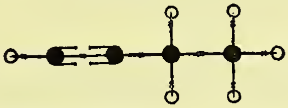
The next members in this homologous series are

Fig. 207



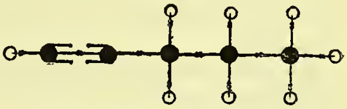
Allylene, methyl-acetylene, $C_3H_4$; a gas

Fig. 208



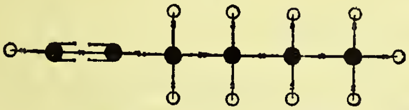
Ethyl-acetylene, $C_4H_6$; b.p. 18°

Fig. 209



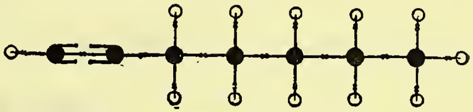
Propyl-acetylene, $C_5H_8$; b.p. 48°

Fig. 210



Hexoylene, $C_6H_{10}$; b.p. 80°

Fig. 211



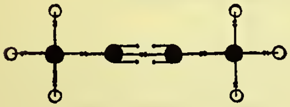
Œnanthylidene, $C_7H_{12}$; b.p. 106°

Several of the higher homologues are also known.

### ISOMERS

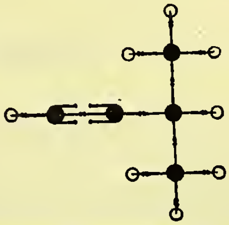
The better known of the isomers of this homologous series are

Fig. 212



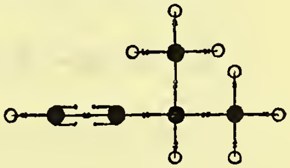
Crotonylene, $C_4H_8$; b.p. 18°

Fig. 213



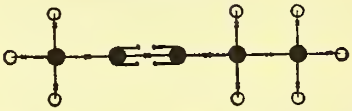
or

Fig. 214



Iso-propyl-acetylene, iso-valerylene (isoprene, *R. & S.* V. p. 491), $C_5H_8$; b.p. 28°

Fig. 215



Valerylene, $C_5H_8$; b.p. 44°

The acetylenes are interesting, too, on account of the change their normal compounds undergo when heated with alcoholic potash. The methyl group at the end of the chain detaches itself and jumps over to the other end, exchanging places with the hydrogen there. This seems to be a general property belonging to all the normal acetylenes (comp. *Ber.* xxv. p. 2243).

The process is thus illustrated:

Fig. 216

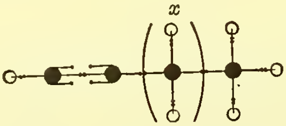
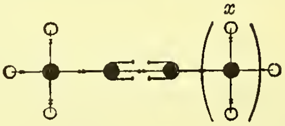


Fig. 217



The exchange taking place inside the molecule itself and not with an outsider (as is commonly the case), the process is termed *intramolecular change*. It is not unfrequently met with in other compounds.

It is characteristic of all trebly bound hydrocarbons that with some metals (copper and silver) they form explosive compounds, but only then, if the triple bond is placed at the extreme end of the chain, as in fig. 216; if the hydrogen-atom is replaced by methyl, ethyl, &c., as in fig. 217, the explosive character disappears. This property often affords a clue to the structure of such compounds.

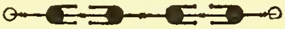
It will be observed that the general formula of the acetylenes, $C_nH_{2n-2}$, is the same as of the di-ethylenes (*vide* p. 37). These two classes are therefore often put together as isomers in the wider sense of the word.

## Di-acetylenes, $C_nH_{2n-6}$

NORMAL

The only known compound of this class is

Fig. 218



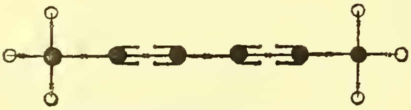
Di-acetylene, $C_4H_2$; a gas

and of the

ISOMERS

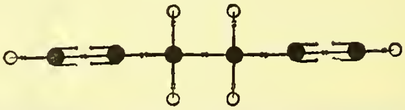
only two are known.

Fig. 219



Di-methyl-di-acetylene, $C_6H_6$; m.p. 64°

Fig. 220



Di-propinyl, di-propargyl, $C_6H_6$; b.p. 85°

These hydrocarbons have the same general formula, $C_nH_{2n-6}$, as the tetra-ethylenes (*vide* p. 21), and both are quite commonly spoken of as isomers. Their relation, however, is the same as between acetylenes and di-ethylenes (see above).

## Tri-acetylenes, $C_nH_{2n-10}$

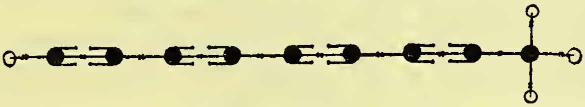
No tri-acetylene of any kind has as yet been recognised as such.

## Tetra-acetylenes, $C_nH_{2n-14}$

Derivatives of only one normal and of one isomeric hydrocarbon are known.

NORMAL

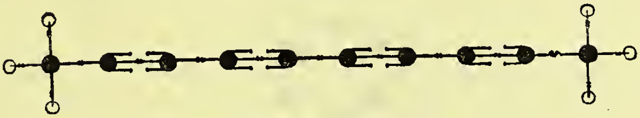
FIG. 221



Methyl-tetra-acetylene, $C_9H_4$

ISOMER

FIG. 222



Di-methyl-tetra-acetylene, $C_{10}H_6$

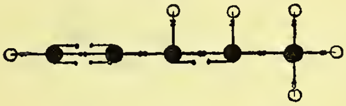
Though there is good authority for the existence of the derivatives from these remarkable hydrocarbons (*Ber*. xviii. pp. 674 and 2269), they have not been analysed, which is a *conditio sine* to the more sceptical fraternity of chemists.

## Mixed double and triple bonds

For the sake of completeness an example of a normal and another of an isomeric hydrocarbon belonging to this class are here illustrated:

NORMAL

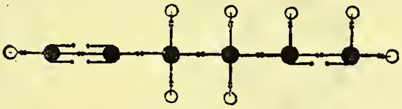
FIG. 223



Valylene, $C_5H_6$; b.p. 50°

ISOMER

FIG. 224



Di-allylene, hexone, $C_6H_8$; b.p. 70°

There are two more hexones whose structures, however, are unknown; probably their double bond takes up a different place in the chain, or they may be iso-compounds, or belong to the tri-ethylenes (*vide* fig. 138, p. 29).

A series of homologues have their names fashioned after hexone: as heptone, $C_7H_{10}$; octone, $C_8H_{12}$, &c.

# CYCLO-HYDROCARBONS

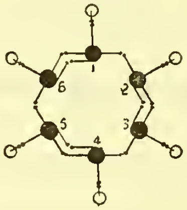
There is no cyclo-hydrocarbon specially calling for our attention beyond those already mentioned on pp. 24–33, until we come to the benzene-ring, where there is a wide field open for speculation.

These cyclo-hydrocarbons have been considered a class distinctly different from the methane group and its derivatives; but we have seen how it is developed from the methane exactly in the same manner as all the rest of hydrocarbons. The class has been termed the *aromatic series* because of the sweet odour of the compounds which were first recognised as belonging to this series. But in course of time it has been found that even this distinction does not hold good, as there are as many bad as sweet smelling compounds in one class as in the other.

In considering them we make benzene our starting-point, regarding all the derivatives as substitution- or combination-products, and not as derived from open chains, for reasons already stated (p. 30).

We will then begin by pointing out that all the links taken singly are perfectly identical, having a double bond on one side, a single on the other, and the fourth valency of each carbon-atom bound to a hydrogen-atom:

Fig. 225



therefore when one of the hydrogen-atoms is substituted by a monad atom of another element, or by any mono-valent radical, it is quite indifferent upon which one it is. If we substitute one of the hydrogen-atoms by methyl, for instance, the product will be the same methyl-benzene, on whichever link we effect the substitution.

But as soon as we substitute two of the hydrogen-atoms by two methyls it is no longer indifferent where the substitution takes place. Three different positions are then possible:

Fig. 226

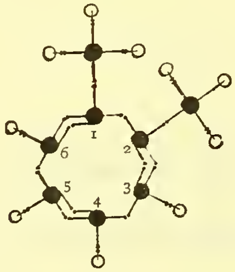


Fig. 227

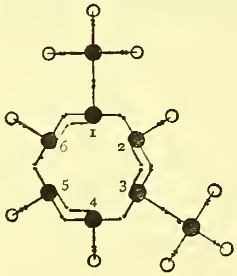
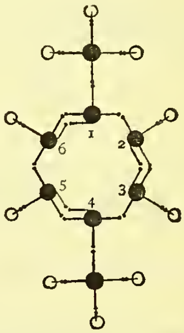


Fig. 228



In the first instance the two carbon-atoms upon which the substitution takes place are neighbours, in the second they are separated by another carbon-atom, and in the third by two. If the methyl be placed on either of the two remaining carbon-atoms one of these relations will be repeated; therefore there are only three different positions in which two substitutes can be placed on a benzene. The first is said to be an *ortho-position*, the second a *meta-position*, and the third a *para-position*. Instead of writing these in full they are generally abbreviated to *o*-, *m*-, *p*-.

Lately it has become perhaps more usual to number the carbon-atoms from one to six, as shown in the figures above, and the expediency of this is particularly noticeable in more complex compounds. Ortho-position would then be designated 1 : 2, 2 : 3, 3 : 4, 4 : 5, 5 : 6, or 6 : 1; meta-position would be 1 : 3, 2 : 4, 3 : 5, 4 : 6, or 1 : 5; similarly para-position would be 1 : 4, 2 : 5, or 3 : 6.

If three hydrogen-atoms in benzene are replaced by the same substituents, there are only three different positions in which they can be placed.

For the purpose of illustration we may again make use of our old acquaintance, methyl:

Fig. 229

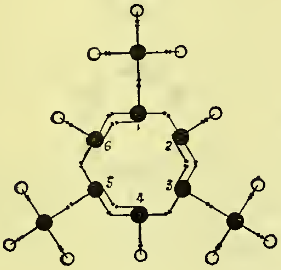


Fig. 230

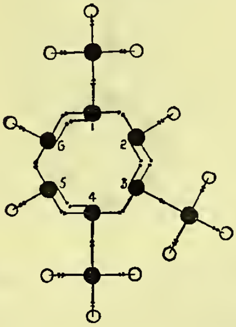
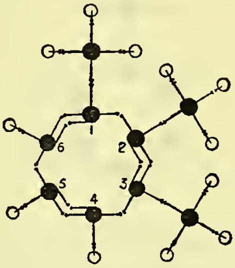


Fig. 231



The first of these positions (1 : 3 : 5) is termed *symmetrical*; the second (1 : 3 : 4) *asymmetrical*; and the third (1 : 2 : 3) *vicinal*. Commonly the initials only (*s*, *a*, *v*) are used.

By combining the two systems all sorts of positions may be accurately described; but the figure system is much simpler and is getting more prevalent.

After these preliminary remarks we can go on describing a few of the more interesting substitution products. Substitutions being nothing more than a joining of radicals, we will for the sake of classification consider these compounds as combinations of radicals.

## A. Combinations with single bonds

| | | |
|---|---|---|
| 1 | Benzene radicals (phenyl, fig. 173, p. 34) and paraffin-radicals | (p. 10) |
| 2 | " " " " " ethylene-radicals | (p. 33) |
| 3 | " " " " " paraffin- and ethylene-radicals | (p. 33) |
| 4 | " " " " " acetylene-radicals | (p. 34) |
| 5 | " " " " " pentaphene-radicals | (p. 28) |
| 6 | " " " " " naphthalene- and paraffin-radicals | (p. 31) |
| 7 | " " " " mutually | |
| 8 | Naphthalenes mutually | |

## B. Combinations with double bonds

| | | |
|---|---|---|
| 1 | Bi-valent benzene radicals (phenylene, fig. 174, p. 34) and paraffin-radicals | |
| 2 | " " " " " " indene- " | (p. 30) |
| 3 | " " " " " " naphthalene-radicals | |
| 4 | " " " " " " naphthalene- and paraffin-radicals | |

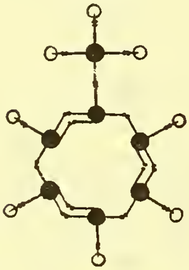
# A. Combinations with single bonds

## 1. Phenyl-paraffins

### *a.* ONE BENZENE AND ONE PARAFFIN

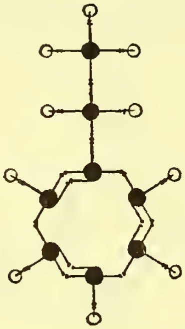
The following may serve as instances of this combination:

Fig. 232



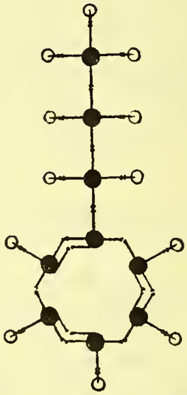
Methyl-benzene, toluene, $C_7H_8$; b.p. 110°

Fig. 233



Ethyl-benzene, $C_8H_{10}$; b.p. 136°·5

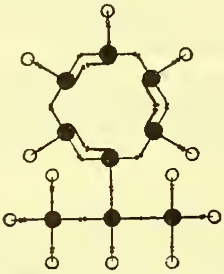
Fig. 234



Propyl-benzene, $C_9H_{12}$; b.p. 157°

These are considered normal compounds because the paraffin-radical is derived from a normal paraffin. When derived from an isomeric paraffin they are termed accordingly

Fig. 235

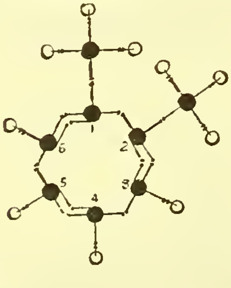


Iso-propyl- (*vide* fig. 32, p. 11) benzene, cumene, $C_9H_{12}$; b.p. 153°

### *b.* ONE BENZENE AND TWO PARAFFINS

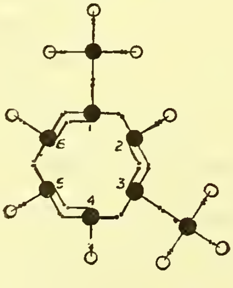
*Two methyls.* There are three possible positions, and they are all known:

Fig. 236



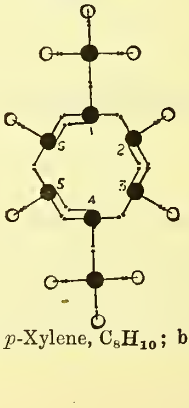
1:2 or *o*-Xylene, $C_8H_{10}$; b.p. 142°; has been used externally in smallpox, erysipelas, &c.

Fig. 237



1:3 or *m*-Xylene, $C_8H_{10}$

Fig. 238

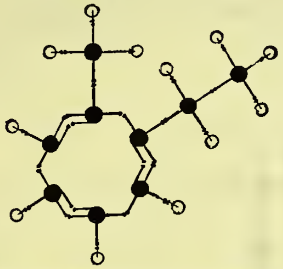


1:4 or *p*-Xylene, $C_8H_{10}$; b.p. 136°

Because they have the same empirical formula as ethyl-benzene, $C_8H_{10}$, they are said to be isomers of that compound.

*Methyl and ethyl.* The three possible isomers of this compound have been prepared. It is sufficient to illustrate one of them:

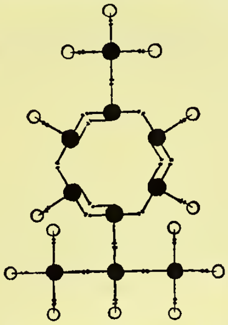
Fig. 239



1 : 2 or *o*-Methyl-ethyl-benzene, *o*-ethyl-toluene, $C_9H_{12}$; b.p. 158°

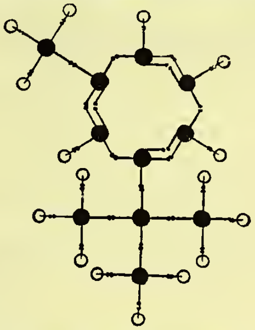
This compound is an isomer of propyl and iso-propyl-benzene in the same sense as the preceding ones were isomers of ethyl-benzene.

Fig. 240.—Methyl and Isopropyl



*p*-Methyl-iso-propyl-benzene (cymene), *vide* fig. 142, p. 29, $C_{10}H_{14}$; b.p. 175°

Fig. 241.—Methyl and Iso-butyl

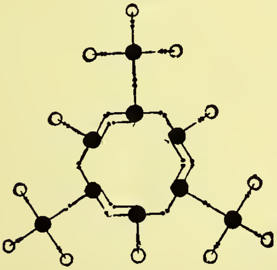


Methyl-*m*-iso-butyl-benzene, $C_{11}H_{16}$; not yet prepared

c. ONE BENZENE AND THREE PARAFFINS

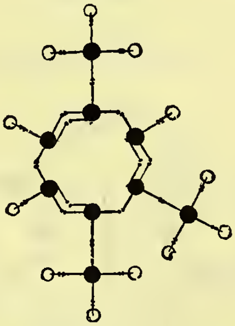
*Three methyls.* Here, again, three combinations are possible, and have all been prepared:

Fig. 242



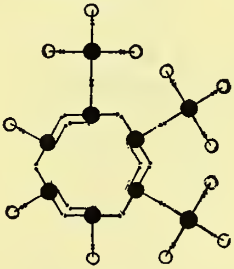
Mesitylene, 1 : 3 : 5 or *s*-tri-methyl-benzene, $C_9H_{12}$; b.p. 164°

Fig. 243



Pseudo-cumene, 1 : 3 : 4 or *a*-trimethyl-benzene, $C_9H_{12}$; b.p. 169°

Fig. 244

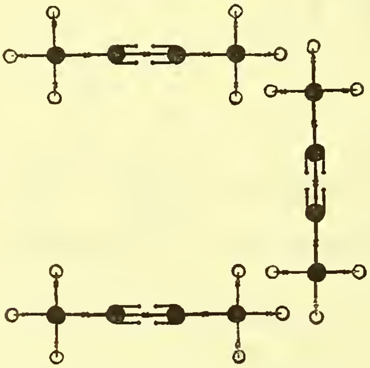


Hemellithene, 1 : 2 : 3 or *v*-trimethyl-benzene, $C_9H_{12}$; b.p. 172°

These are, again, on account of their empirical formulæ, $C_9H_{12}$, said to be isomers of ethyl-toluene, fig. 239, propyl-benzene, fig. 234, and iso-propyl-benzene, fig. 235.

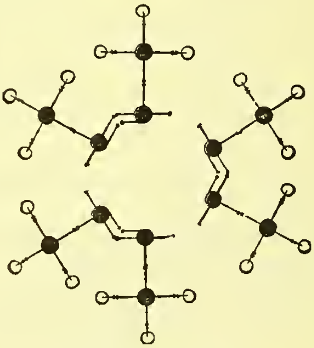
As benzene can exchange every one of its hydrogen-atoms for paraffin-radicals, there are still a great number of normal and isomeric compounds that need not be mentioned here, except one, viz. *mellitene*, that being interesting on account of its formation from crotonylene (fig. 212, p. 39) through polymerisation, exactly in the same way as benzene was formed from acetylene (*vide* p. 32).

Fig. 245



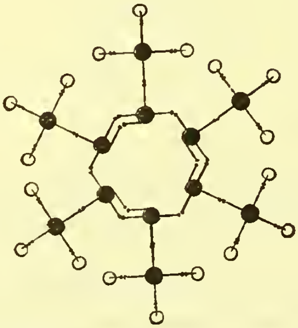
Three molecules of crotonylene

Fig. 246



Triple bonds broken

Fig. 247

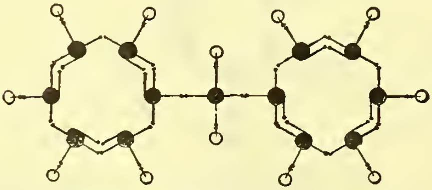


Hexa-methyl-benzene, mellitene, $C_{12}H_{18}$; m.p. 164°

## *d.* DI-PHENYL-PARAFFINS

*Benzenes and methane:*

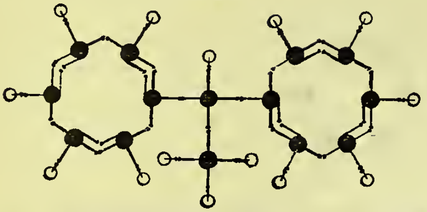
Fig. 248



Di-phenyl-methane, $C_{13}H_{12}$; m.p. 26°

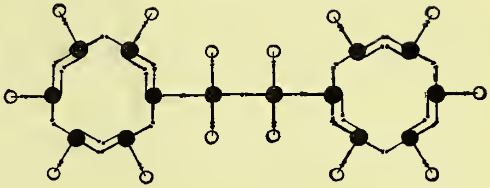
*Benzenes and ethane:*

FIG. 249



Asymmetric di-phenyl-ethane, $C_{14}H_{14}$; b.p. 268°

FIG. 250

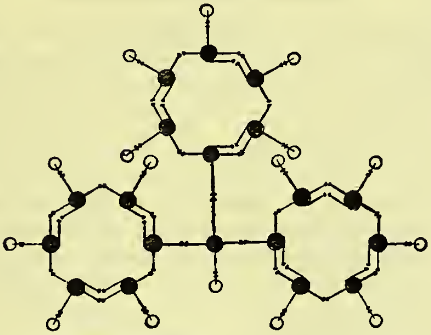


Symmetric di-phenyl-ethane, di-benzyl, $C_{14}H_{14}$; m.p. 51°·5

### *e.* TRI-PHENYL-PARAFFINS

*Benzenes and methane:*

FIG. 251



Tri-phenyl-methane, $C_{19}H_{16}$; m.p. 92°

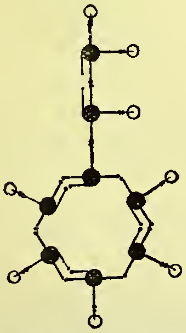
Mother substance of an extensive series of dyes: *bitter-almond-oil-green, rosanilin, fuchsin, methyl-violets, methyl-green, spirit-blue, aurin eosin,* &c.

There is also a combination of ethane with four benzenes, *tetraphenyl ethane,* the structure of which is in perfect analogy to the others.

## 2. Phenyl-ethylenes

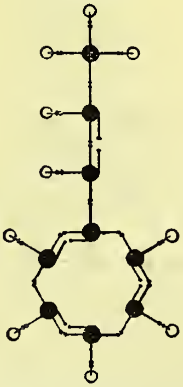
### *a.* ONE BENZENE AND ETHYLENE

FIG. 252.



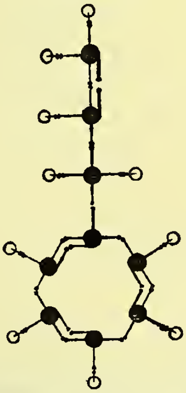
Vinyl- (fig. 164, p. 33) benzene, phenyl-ethylene, styrolene, styrene, cinnamene, $C_8H_8$; b.p. 146°; occurs in storax (*Styrax off.*)

FIG. 253



Phenyl-propylene (fig. 165, p. 33), $C_9H_{10}$; b.p. 165°

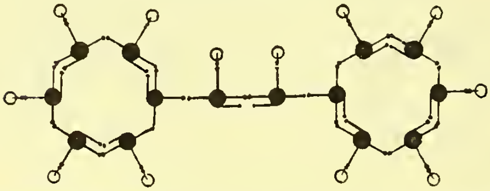
FIG. 254



Phenyl-allyl (fig. 167, p. 33), $C_9H_{10}$; b.p. 155°

### *b.* TWO BENZENES AND ETHYLENE

Fig. 255



Stilbene, toluylene, di-phenyl-ethylene, $C_{14}H_{12}$; m.p. 120°; mother substance of the cotton dyes

## 3. Benzenes, paraffins, and ethylenes

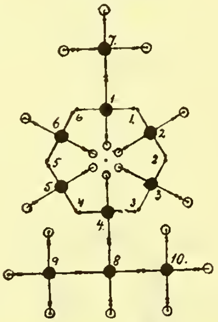
## TURPENTINE OILS

### TERPENES AND CAMPHENES

A paraffin residue, frequently found to replace a hydrogen-atom in benzene, or rather in toluene (fig. 232, p. 44), is iso-propyl (figs. 32 and 34, p. 11), or one of its immediate derivatives. We have already referred to two such substitution-products (cymene, fig. 142, p. 29, and limonene, or, according to later researches, terpinene, fig. 144, p. 29); many similar hydrocarbons are present, either as such or as derivatives, in turpentine and other ethereal oils and in camphors, or are laboratory products. The general features of their structures are pretty well agreed upon, but of the details so much diversity of opinion has existed that there is scarcely another class of organic compounds of which such confusion has been made as of the turpentine oils; it is only recent investigations (*Ber.* xxiv., xxvi., and xxvii.) that have thrown a definite light upon some of them. It may, therefore, perhaps be interesting to look into the matter a little more fully than the strict purpose of this treatise otherwise would warrant, and we shall to some extent do so again when we afterwards have to discuss their derivatives.

The turpentine oils may be divided into two classes, terpenes and camphenes, both of the empirical formula $C_{10}H_{16}$, and both derivable from hexa-hydrated cymene by abstracting one or two pairs of hydrogen-atoms, either from the ring, or from the side-chain, or from both, creating either double bonds, as before explained, or a new kind of bonds, described later on. If all hydrogen-atoms are removed in pairs from *neighbouring* carbon-atoms, terpenes are formed; but if one of the pairs is removed from carbon-atoms in *para-positions*, camphenes are formed. In order to distinguish the various carbon-atoms and bonds, they are numbered as under:

Fig. 257



Cymene-hexa-hydride, $C_{10}H_{20}$; b.p. 171°–173°

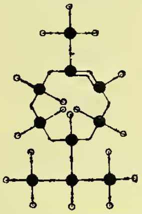
For the purpose of designating the position of a double bond, the Greek capital Δ is employed, followed by the numeral of the bond or bonds, as indicated in the figure above, and in the case of a double bond connecting the side-chain with the ring, the numeral of the ring-carbon is followed, in parentheses, by the numeral of the carbon in the side-chain; the bond connecting carbon-atoms in para-, or any other, position, for the designation of which no proposal has been made, may, for our purpose, be indicated by the numeral of the carbon-atoms thus connected placed in form of a fraction.

## Terpenes

In formation of terpenes one or two pairs of hydrogen-atoms are removed from neighbouring carbon-atoms: one pair is always removed from carbon-atoms in the ring; when two pairs are removed, both are, in most cases, abstracted from ring-carbons; but in one case, at least, one is abstracted from the ring and the other from neighbouring carbon-atoms, one of which is in the ring, the other in the side-chain.

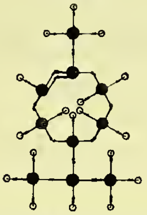
When we abstract one pair of hydrogen-atoms from cymene hexa-hydride, a tetra-hydride is formed; by removing each time a different pair of hydrogen-atoms, six tetra-hydrides may be formed, each of which, however, will always correspond to one of the others. We will, for instance, illustrate the two compounds formed when we remove a pair of hydrogens from carbons 1 and 2, and from carbons 1 and 6.

Fig. 258



$\Delta^1$ Cymene-tetra-hydride

Fig. 259

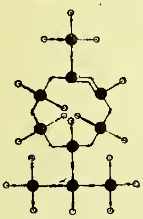


$\Delta^6$ Cymene-tetra-hydride

As long as there is no discrimination between fronts and backs of these two figures, they are evidently identical, the one seen from the back of the paper being exactly the same as the other from the opposite direction. But supposing the two figures are moving towards the observer, fronts and backs have to be recognised, and then at once a difference is apparent, the double bond being in one figure on the right-hand side, in the other on the left. Now, it is a fact that amongst terpenes and camphenes two compounds have nearly always been found to have the same chemical behaviour, but to differ in some such physical property as the boiling or melting point; principally, however, in their action on polarised light, one turning it in one direction, the other in the opposite direction, for which reason they are termed dextro- and lævo-compounds of the terpene in question. The cause of this difference will be more fully discussed afterwards (p. 463); for the present, the above explanation will suffice to make it intelligible that there may be a difference, though we cannot, with our diagrams, indicate it better than by the two figures above. Just as these two, $\Delta^1$ and $\Delta^6$, correspond, so do $\Delta^2$ and $\Delta^5$, $\Delta^3$ and $\Delta^4$. There are, therefore, three cymene-tetra-hydrides, each with a corresponding compound, viz.

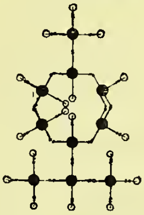
CYMENE-TETRA-HYDRIDES

Fig. 260



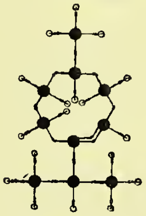
$\Delta^1$ corresp. to $\Delta^6$

Fig. 261



$\Delta^2$ corresp. to $\Delta^5$

Fig. 262



$\Delta^3$ corresp. to $\Delta^4$

We shall now see which compounds have been assigned to them respectively.

$\Delta^1$ and $\Delta^6$, fig. 260: Carvo-menthene, $C_{10}H_{16}$, b.p. 174°·5.

$\Delta^3$ and $\Delta^4$, fig. 262: Menthene, $C_{10}H_{16}$; dextro-compound, b.p. 167°·5; lævo-compound, b.p. 170°–171°.

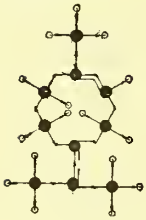
The correctness of these structures has been placed beyond reasonable doubt (*Ber.* xxvi. p. 825).

$\Delta^2$ and $\Delta^5$, fig. 261: Structures have been suggested as those of menthene (*Ber.* xxi. p. 459, and xxv. p. 144), but that suggestion can now scarcely be supported; no other, at present, known compound has been represented by fig. 261. Carvo-menthene and menthene do not occur in nature; they are laboratory products.

When we remove two pairs of hydrogen-atoms from cymene-hexa-hydride, di-hydrides are generally produced; but intermediate links, *tri-hydrides*, are formed by removing one of these pairs, partly from the ring and partly from the side-chain, i.e. from carbon-atoms 4 and 8; or by removing two hydrogens from *one* carbon-atom in the ring:

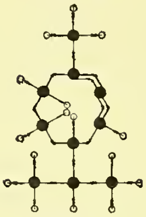
### CYMENE-TRI-HYDRIDES

FIG. 263



$\Delta^{1\cdot4\,(8)}$

FIG. 264



$\Delta^{1\cdot2}$

$\Delta^{1\cdot4\,(8)}$, fig. 263: Terpinolene, $C_{10}H_{16}$, b.p. 183°–185°, has no action on polarised light (inactive).

The above structure has, with great probability of correctness, been assigned to the compound known by this name (*Ber.* xxvii. p. 448). Earlier researches (*Ber.* xxi. p. 172, and xxiv. p. 1575) gave it the structure of fig. 265.

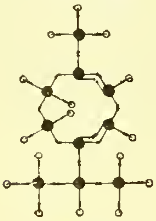
$\Delta^{1\cdot2}$, fig. 264: Sylvestrene, $C_{10}H_{16}$, b.p. 175°–176° (*Ber.* xxi. p. 172), occurs in Scandinavian and Russian turpentine.

The structure $\Delta^{2\cdot3}$ has also been suggested, but, for reasons stated on p. 456, neither is very probable.

### CYMENE-DI-HYDRIDES

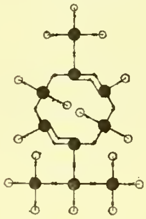
are formed, as stated, by removing two pairs of hydrogen-atoms, each from two different but neighbouring pairs of carbon-atoms in the ring. Five different arrangements of the double bonds are possible besides a corresponding structure to each of the first four of the following:

FIG. 265



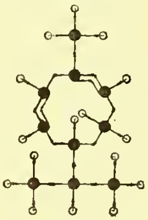
$\Delta^{1\cdot3}$ corr. to $\Delta^{4\cdot6}$

FIG. 266



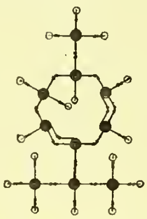
$\Delta^{1\cdot4}$ corr. to $\Delta^{3\cdot6}$

FIG. 267



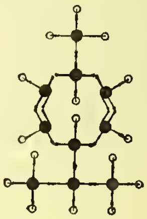
$\Delta^{1\cdot5}$ corr. to $\Delta^{2\cdot6}$

FIG. 268



$\Delta^{2\cdot4}$ corr. to $\Delta^{3\cdot5}$

FIG. 269



$\Delta^{2\cdot5}$

$\Delta^{1\cdot3}$ and $\Delta^{4\cdot6}$, fig. 265: Limonene, $C_{10}H_{16}$; dextro-limonene (*citrene, carvene, hesperidene*), b.p. 175°–176°; lævo-limonene, same b.p.

The former occurs in a great many ethereal oils; the latter is found in some kinds of turpentine oil.

Di-pentene (*inactive limonene, cinene, cajeputene, di-isoprene, iso-terebentene, caoutchin, di-valerylene*), $C_{10}H_{16}$, b.p. 180°–182°.

It occurs in Scandinavian and Russian oils of turpentine, but has also been prepared by mixing equal parts of the two limonenes, and is therefore generally looked upon as consisting of an equal number of dextro- and lævo-limonene molecules, and has consequently no action on polarised light, the two limonenes neutralising each other. Its structure has been conclusively proved to be $\Delta^{1\cdot3}$ or $\Delta^{4\cdot6}$ (*Ber.* xxvii. p. 450).

The same structure was formerly attributed to terpinolene, fig. 263 (*Ber.* xxi. p. 172), and also to iso-terpene (fig. 267) (*Journ. d. russ. ch. G.* xv. p. 471). To limonene the structures, figs. 266, 267, 268, and 269, have at various times also been given, as explained below.

$\Delta^{1\cdot4}$ or $\Delta^{3\cdot6}$, fig. 266, is ascribed by one of the authorities (*Ber.* xxi. p. 169) to limonene, but that interpretation must now be abandoned, and there is no other known terpene to take its place.

$\Delta^{1\cdot5}$ or $\Delta^{2\cdot6}$, fig. 267: Iso-terpene, $C_{10}H_{16}$ (*Ber.* xxi. p. 171); the dextro-compound, b.p. 178°·3, and the lævo-compound, b.p. 175°.

The two iso-terpenes are by some authorities (*Ann.* ccxvi. p. 236) supposed to be the optically active modifications of *terpinolene*, as represented by fig. 265; but if fig. 263 is the true representation of this compound—and there is scarcely room for doubt—and if the theories to be afterwards (p. 462 &c.) submitted are correct, the structure of terpinolene does not admit of any active modifications. So-called iso-terebentenes are probably identical to iso-terpenes. The same structure

$\Delta^{1\cdot 5}$ or $\Delta^{2\cdot 6}$ was formerly ascribed to limonene, fig. 265 (*Ber.* xxiv. p. 1565), and has also been prognosticated as that of an, as yet, hypothetical terpinene (fig. 268) of a rather higher b.p. (*Ber.* xxvii. p. 453).

$\Delta^{2\cdot 4}$ or $\Delta^{3\cdot 5}$, fig. 268: Terpinene, $C_{10}H_{16}$, b.p. 174° (*Ber.* xxvii. p. 453), optically inactive.

This structure has been ascribed also to limonene (*Ber.* xx. p. 492), whilst on the other hand an altogether different one ($\Delta^{\frac{1}{4}\cdot\frac{8}{9}}$, fig. 275) has been suggested for terpinene.

$\Delta^{2\cdot 5}$, fig. 269, has been variously made to represent pinene (*Ber.* vi. p. 439) and dipentene (*Ber.* xxi. p. 169), but the constitutions of those compounds, as represented by figs. 271 and 265 respectively, are more probable, and therefore no compound at present corresponds to fig. 269.

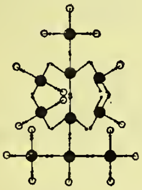
## Camphenes (Pinenes)

Terpenes, it will be remembered, were formed from cymene-hexa-hydride by removing hydrogens in pairs from *neighbouring* carbon-atoms; in the formation of camphenes, one of the pairs to be removed is attached to two carbon-atoms in para-positions, creating by their removal a diagonal bond, characteristic of the class. In representing this bond pictorially, we are obliged to draw the two respective carbon-atoms together a little, inside the regular hexagon, in order to preserve the lengths of the valencies. For all known compounds belonging to this class only one double bond besides the diagonal bond has been suggested, and thus they may be subdivided into two groups, according as the double bond is inside or outside the ring.

### *a.* CAMPHENES WITH THE DOUBLE BOND INSIDE THE RING

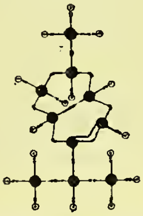
Only three different arrangements are possible when the hydrogen-atoms are removed from different carbon-atoms:

Fig. 270



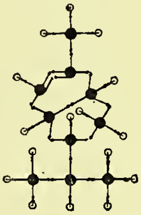
$\Delta^{\frac{1}{4}\cdot 2}$ corresp. to $\Delta^{\frac{1}{4}\cdot 5}$

Fig. 271



$\Delta^{\frac{2}{5}\cdot 3}$ corresp. to $\Delta^{\frac{3}{6}\cdot 4}$

Fig. 272



$\Delta^{\frac{2}{5}\cdot 6}$ corresp. to $\Delta^{\frac{3}{6}\cdot 1}$

$\Delta^{\frac{1}{4}\cdot 2}$ and $\Delta^{\frac{1}{4}\cdot 5}$, fig. 270: Camphene, $C_{10}H_{16}$ (*Ber.* xxiv. p. 1555, and xxv. p. 169); a dextro- (m.p. 48°–54°), a lævo- (*terecamphene*, m.p. 45°–48°), and an inactive form (m.p. 47°) are known.

The same structure has by another authority (*Journ. d. russ. ch. G.* xv. p. 471) been assumed to represent pinene (fig. 271); on the other hand, camphene's constitution has been interpreted also in another way (*vide* fig. 273).

$\Delta^{\frac{2}{5}\cdot 3}$ and $\Delta^{\frac{3}{6}\cdot 4}$, fig. 271: Pinene, *terebentine* (*Ann.* ccxxxix. p. 49, *Ber.* xxi. p. 469, xxv. p. 1112) exists in the three optically different forms as dextro-pinene, *australene*, b.p. 156°, lævo-pinene, *terebentene*, b.p. 155°–156°, and inactive pinene, b.p. 155°–156°.

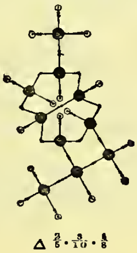
The two former are the chief constituents of different oils of turpentine. Other structures suggested for pinene are figs. 269, 270, and 272, besides several more, including some with open chains that need not be illustrated here (*Ber.* xi. pp. 152 and 1698, xxiv. p. 2188, *Journ. d. russ. ch. G.* x. p. 315).

$\Delta^{\frac{2}{5}\cdot 6}$ and $\Delta^{\frac{3}{6}\cdot 1}$, fig. 272. This structure has been given to pinene (*Ber.* xxiv. p. 1539) in preference to fig. 271, formerly suggested by the same authority (*Ann.* ccxxxix. p. 49).

Somewhat related to this group is a structure suggested for camphene (*vide* fig. 270), in which the iso-propyl-radical is bound to the ring by two of its valencies.

It is interesting as a connecting link between this group and the following one, in which iso-propyl is converted into propenyl or allyl. For a correct interpretation of this and other structures with diagonal bonds, see p. 53 and figs. 595 and 596, p. 144.

Fig. 273

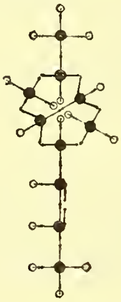


$\Delta^{\frac{2}{5}\cdot\frac{3}{10}\cdot\frac{4}{8}}$

### *b.* CAMPHENES WITH THE DOUBLE BOND OUTSIDE THE RING

We know but three compounds for which structures of this kind have been suggested:

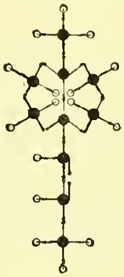
Fig. 274



$\Delta^{\frac{2}{5}\cdot\frac{8}{9}}$

Phellandrene, $C_{10}H_{16}$; b.p. 171–172°
(*Ber.* xxi. p. 175)

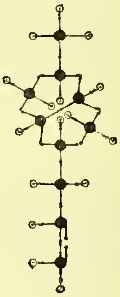
Fig. 275



$\Delta^{\frac{1}{4}\cdot\frac{8}{9}}$

Terpinene, $C_{10}H_{16}$; b.p. 179–181°
(*Ber.* xxi. p. 175, xxiv. p. 1577);
see also text to fig. 268

Fig. 276



$\Delta^{\frac{2}{5}\cdot\frac{9}{10}}$

Laurene, $C_{10}H_{16}$; b.p. 173°
(*Ber.* xxi. p. 176)

*Oil of turpentine.* The French oil consists almost entirely of lævo-pinene, which also occurs in Venice turpentine and Canada balsam. Dextro-pinene is contained in American and Scotch oils and sylvestrene (see p. 48), in conjunction with di-pentene in Scandinavian and Russian oils of turpentine, obtained from the roots of *Pinus sylvestris.*

*Terebene* is oil of turpentine distilled with 5-per-cent. concentrated sulphuric acid, washed with diluted solution of sodium carbonate, treated with chloride of calcium, and again distilled, being converted chiefly into dipentene, having an odour of thyme and terpineol with a dash of hyacinths (*vide* fig. 436, p. 98). Used as a disinfectant and antiseptic, and for inhalation in bronchitis and winter-cough.

*Dextro-limonene* is a constituent of the oils of orange-rind, of dill, lemon, bergamot, caraway, and of many other oils.

*Lævo-limonene*, together with lævo-pinene, is present in the oil of fir cones.

*Dipentene* is found in the ethereal oil of the camphor tree. All terpenes are converted into dipentene through the action of sulphuric acid, and into cymene by iodine. *Phellandrene* is present in the ethereal oil of *Phellandrum aquaticum*, elemi and eucalyptus oils.

All the other terpenes are laboratory products.

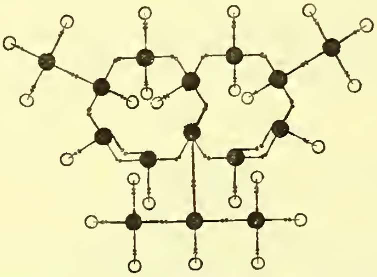
*Retinol, resinol*, or *rosinol* is a liquid from destructive distillation of resin, consisting of hydrocarbons of various constitutions. It is used for blenorrhœa, and is an excellent solvent for iodol, aristol, camphor, chrysophanic acid, cocaïne, codeïne, strychnine, carbolic acid, creosote, and phosphorus.

*Catramin* is turpentine derived from *Abies canadensis balsamica.* Used for tuberculosis and lupus as subcutaneous injection, and as embrocation; also internally, and as vapour for inhalation.

### SESQUI-, DI-, AND POLY-TERPENES

Terpenes and camphenes may be considered formed from two molecules of isoprene, $C_5H_8$, by *polymerisation*, or *spontaneous transformation*, in a similar way as we have seen benzene formed from three molecules of acetylene, p. 32; the structure of isoprene is, however, not sufficiently known, and the process can therefore not be illustrated; but fig. 278 is a suggested structure of a sesqui-terpene.

Fig. 278



Cadinene, $C_{15}H_{24}$, b.p. 274° (*Ann.* ccxxxix. p. 49)

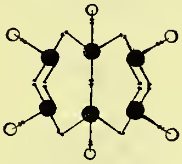
This spontaneous transformation is not limited to two molecules of isoprene; three, four, or more molecules may unite, and the produce is termed *sesqui*-($C_{15}H_{24}$), *di*-($C_{20}H_{32}$), or *poly-terpenes* ($C_{5n}H_{8n}$). Colophen is a di-terpene; caoutchouc and gutta-percha, poly-terpenes. Indiarubber is said to have formed spontaneously from isoprene (*Ch. & D.* xl. p. 870); and as turpentine may be converted into that compound, a possibility is opened for making indiarubber from turpentine.

## THE DIAGONAL BOND

We meet with this mode of binding for the first time in the terpenes, and it requires therefore a few words of explanation.

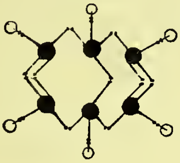
The hexagon is by this bond, as it were, cut in halves.

Fig. 279



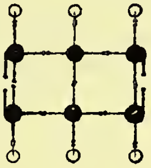
It will be seen that the benzene-ring has changed into two interlocked rings of four carbon-atoms each, of which two are common to both rings. If we stretch out the valencies of each ring in order to get symmetrical figures we obtain this structure:

Fig. 280



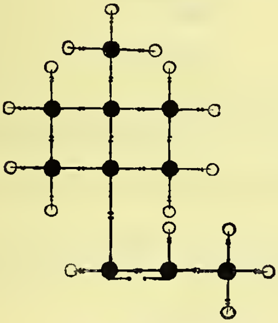
which may, perhaps, better be drawn thus:

Fig. 281



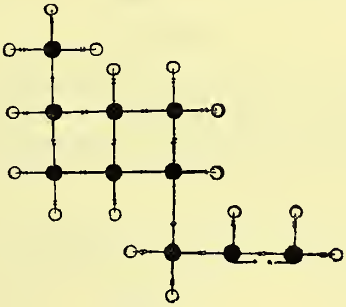
Terpinene and laurene, for instance, would then have these forms:

Fig. 282



Terpinene

Fig. 283

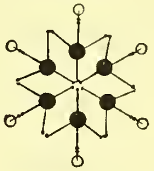


Laurene

showing plainly that these compounds are condensed tetra-methylenes (*vide* fig. 120, p. 25), and no longer benzene derivatives.

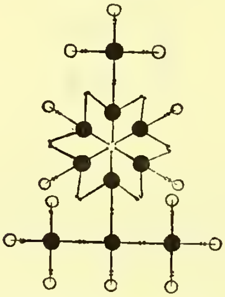
The idea of the diagonal bond has found so much favour with some chemists that they have applied it to the benzene itself, making of all the double bonds diagonal ones—

Fig. 284



in accordance with which cymene (fig. 142, p. 29) would assume such form (vide *Ber.* xxv. p. 1111):

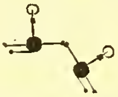
Fig. 285



This is called Claus's ring, the other one being Kekulé's, named after their propounders. Several others have been proposed, with cross bindings in all directions; but Kekulé's formula is the one by which most reactions can be explained without too much strain. Some properties of benzene-compounds (refractive power and specific volume) lead to the conclusion that three double bonds exist, but other properties (heat of combustion) prove that there are only single bonds present.

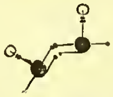
To add to our trouble the positions 1 : 2 and 1 : 6 are, in point of fact, identical; there is no doubt about that; but it is difficult to see why they are so when they look so different—

Fig. 286



Position 1 : 2

Fig. 287



Position 1 : 6

being in the first instance bound by single, in the second by double linkage.

Kekulé has tried to solve the problem by assuming a theory, now generally accepted, that the atoms are not stationary, but continually in motion.

Though not exactly Kekulé's notion, the following explanation may serve as a popular form for the idea.

The second linkages in the benzene ring are moving like pendulums, striking alternately their neighbours to the right and to the left. Consequently the ring will have alternately one of these two forms:

Fig. 288

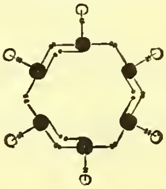
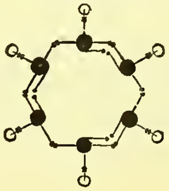


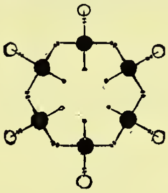
Fig. 289



Then, of course, there will be no difference as regards the positions 1 : 2 and 1 : 6, and it will make no difference in which of these positions we draw the double bonds. There are several instances of such re-arrangements of the bonds in compounds which we are going to consider by-and-by.

On their way from one side to the other there will be a moment when all second linkages will point towards the centre.

Fig. 290



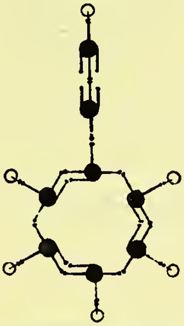
In this way everyone gets his due, should thank the gods, and rest content.

The latest views on this subject cannot be discussed here, but will be found on p. 482.

## 4. Benzenes and Acetylenes

### *a.* ONE BENZENE AND ACETYLENE

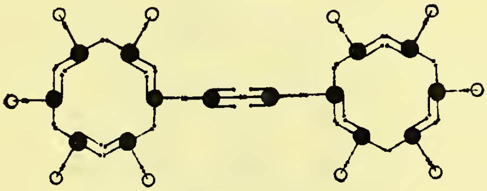
Fig. 291



Phenyl-acetylene, $C_8H_6$; b.p. 140°

### *b.* TWO BENZENES AND ACETYLENE

Fig. 292

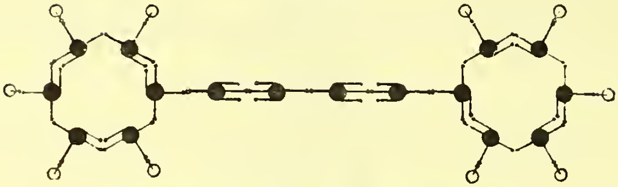


Tolane, diphenyl-acetylene, $C_{14}H_{10}$; m.p. 60°

is formed from *stilbene* (fig. 255, p. 48) by abstraction of two hydrogen-atoms.

### c. TWO BENZENES AND DI-ACETYLENE

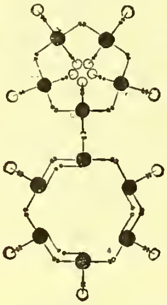
Fig. 293



Di-phenyl-di-acetylene, $C_{16}H_{10}$; m.p. 97°

## 5. Benzene and Pentamethylene

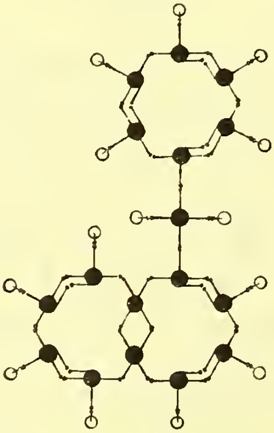
Fig. 294



Phenyl-pentamethylene, $C_{11}H_{14}$; hypothetical. Theoretical derivatives: **antipyrin, oxycarbamil, &c.**

## 6. Benzene, paraffin, and naphthalene

Fig. 295

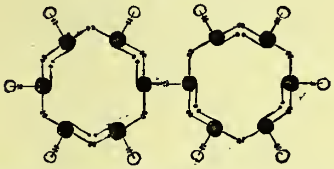


Benzyl-naphthalene, $C_{17}H_{14}$; m.p. 58°·6. Theoretical derivatives: **narcotine, hydrastine**

## 7. Benzene and derivatives mutually

### *a.* TWO BENZENES:

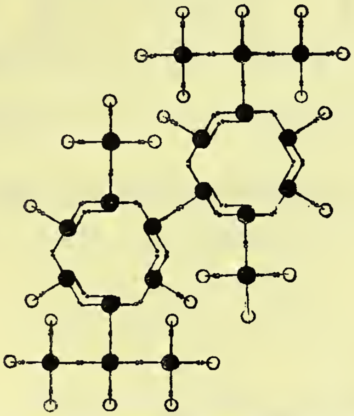
FIG. 296



Di-phenyl, phenyl-benzene, $C_{12}H_{10}$; m.p. 71°

### *b.* TWO CYMENES (fig. 240, p. 45)

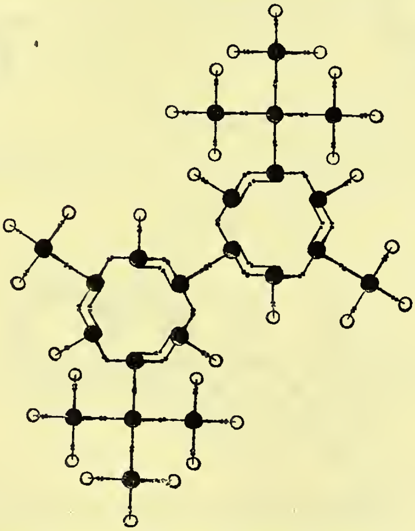
FIG. 297



Di-cymene, $C_{20}H_{26}$; not yet prepared. Derivatives: aristol and carvacrol

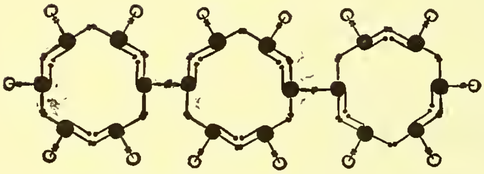
### *c.* TWO METHYL-*m*-ISO-BUTYL-BENZENES (fig. 241, p. 45)

FIG. 298



Di-methyl-di-*m*-iso-butyl-di-benzene, $C_{22}H_{30}$; not yet prepared. Derivative: europhene *d.* THREE BENZENES

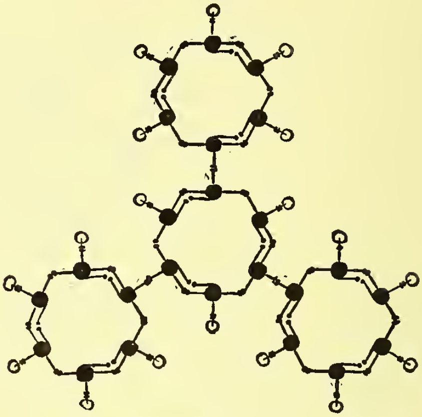
Fig. 299



Di-phenyl-benzene, $C_{18}H_{14}$; m.p. 205°

*e.* FOUR BENZENES

Fig. 300

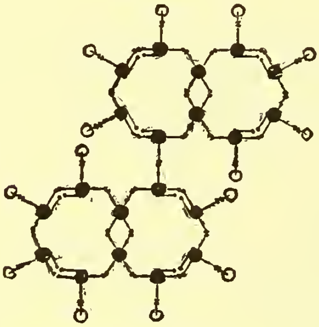


Tri-phenyl-benzene, $C_{24}H_{18}$; m.p. 170°

## 8. Naphthalenes mutually

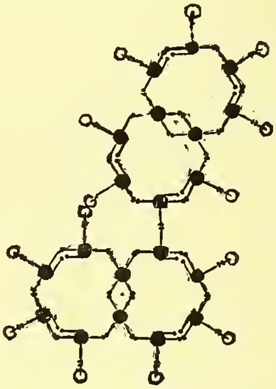
Two naphthalenes may be united in different ways. Here are three of them:

Fig. 301



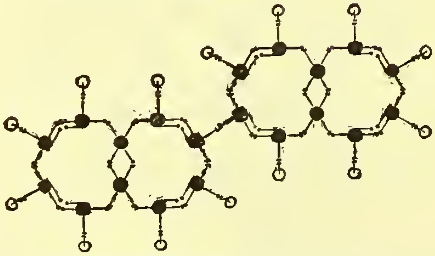
*a*-*a*-di-naphthalene, $C_{20}H_{14}$; m.p. 154°; theoretical derivatives: quinine, cinchonine; *vide* p. 410

Fig. 302



*a*-*β*-di-naphthalene, $C_{20}H_{14}$; m.p. 76°

Fig. 303



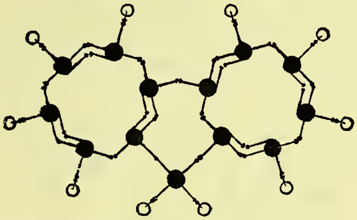
*β*-*β*-di-naphthalene, $C_{20}H_{14}$; m.p. 187°

# B. Combinations with double bonds

## 1. Di-valent benzene-radicals (phenylene) and paraffin-radicals

### *a.* TWO PHENYLENES AND METHANE

Fig. 304

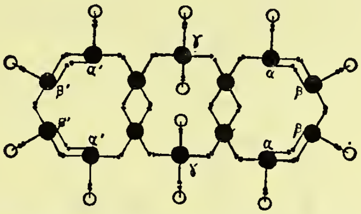


Fluorene, di-phenylene-methane, $C_{13}H_{10}$ ; m.p. 112°

is present in coal-tar, crystallises in plates with a beautiful violet fluorescence.

### *b.* TWO PHENYLENES AND TWO METHANES

Fig. 305



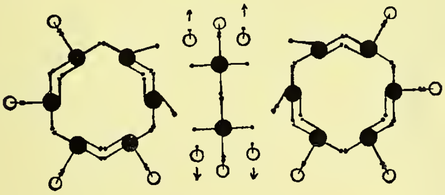
Anthracene di-hydride, $C_{14}H_{12}$ ; m.p. 107°

may also be regarded as three condensed benzene-nuclei, of which the one in intermediate position is hydrated, i.e. two hydrogen-atoms added.

### *c.* TWO PHENYLENES AND ETHANE

The three radicals combine in this manner:

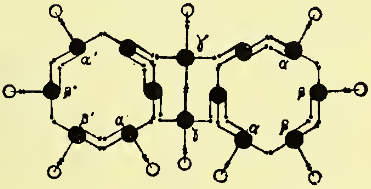
Fig. 306



Phenylene ethane less four hydrogen atoms (acetylene) phenylene

=

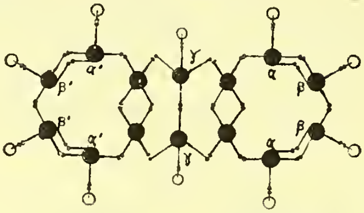
Fig. 307



= Anthracene, $C_{14}H_{10}$ ; m.p. 213° ; colourless plates with magnificent blue fluorescence ; mother-substance of many important dyes—alizarin, purpurin, rufol, &c.

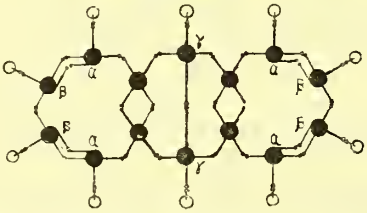
or represented by the diagonal bond

Fig. 308



Anthracene is generally represented as a compound consisting of three condensed benzene-nuclei.

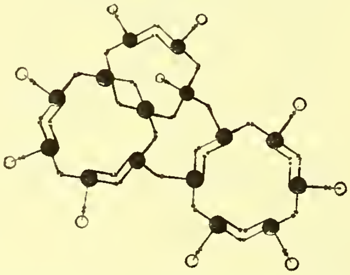
Fig. 309



This is, however, misleading, as it is really two phenylenes united through the agency of ethane, or perhaps rather acetylene. The formation of anthracene from benzene and ethylene direct indicates its constitution; it may also be looked upon as derived from asymmetrical di-phenyl-ethane by removal of four hydrogen-atoms (*vide* fig. 249, p. 47).

## 2. Benzene and indene

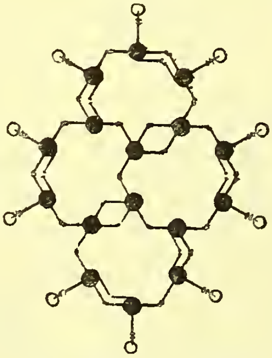
Fig. 310



Fluoranthene, idryl, $C_{15}H_{10}$; m.p. 109°

## 3. Benzene and naphthalene

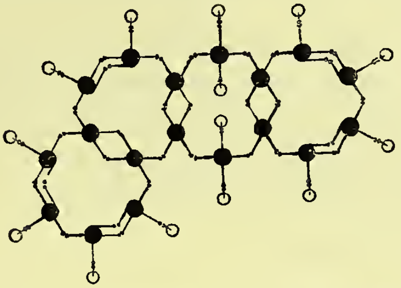
Fig. 311



Pyrene, $C_{16}H_{10}$; m.p. 148°

### 4. Benzene, naphthalene, and paraffin

Fig. 312



Di-methyl-phenylene-naphthalene, $C_{18}H_{14}$; hypothetical. Theoretical derivatives: morphine, codeïne, &c.

## The Nomenclature of the Future

Though this question is still pending it may perhaps interest the reader to know something of it.

The nomenclature of hydrocarbons with open chain may be considered settled in its main feature; the proposal laid before the Congress at Geneva is merely an enlargement of a system which, originally proposed by the late Professor A. W. Hofmann, has slowly but surely been gaining more and more ground. It is founded on the principle which it is intended to apply to the whole nomenclature, that a systematic name should in every instance indicate the structural formula and the character of the respective compounds.

Accordingly it was proposed that all hydrocarbons should be known by the number of the carbon-atoms by which the straight chain in the structure of the respective compounds is represented by the law of atomic linking, the number being expressed by the Greek designations of the numerals; in the presence of side-chains where several interpretations are possible, that by which the longest straight chain can be formed is to be chosen; for instance, the structure of pseudo-pentane may be looked upon in two different ways, as represented either by fig. 56 or by fig. 57, p. 14: the first of these is represented by a straight chain of four carbon-atoms, and is therefore to be chosen in preference to the other, the straight chain of which consists of three carbon-atoms only.

The saturated compounds are to be distinguished by the suffix *-ane*, those with double bonds by *-ene*, with triple bonds by *-ine*, and those with mixed double and triple bonds by *-enine*, but probably not considering such bonds in side-chains.

When we, however, come to the application of these excellent rules, we start with four exceptions: methane, ethane, propane, and butane, with their suffixes *-ene* and *-ine* (and *-enine* in the case of butane), will retain their old names, but the rest of the hydrocarbons will strictly follow the rules; pentane, pentene, pentine, pentenine, hexane, hexene, hexine, hexenine, &c.

The carbon-atoms are to be distinguished by their ordinal number in the straight part of the chain, commencing in asymmetrical structures from the end most proximate the asymmetrical cause; in case the asymmetry wholly or partly arises from side-chains, the numbering is always regulated by them, and if two of them are symmetrically placed but of different structures, that end is to be chosen which is nearest the simpler of the two, and in case of simultaneous presence of a double and a triple bond in straight chains, without side-chains, the numbering is to commence from the end nearest to the highest bond.

The positions of double and triple bonds are to be indicated by numeral of the lowest numbered of the two carbon-atoms connected by such bond, and the number of bonds in a chain is indicated by prefixing the terminations *-ene*, and *-ine* by *di-*, *tri-*, &c.; e.g. *diene*, *diine*, *triene*, &c.

The positions of side-chains are to be indicated by the number of the carbon-atom to which they are attached, and in the case of two side-chains being attached to the same carbon-atom, the number of the simpler is to be indexed.

The mutual order of carbon-atoms in side-chains is indicated by indexing numerals, *e.g.* $2^1$, $2^2$, $2^3$, &c., commencing with the atom attached to the main chain.

Side-chains are looked upon as radicals of hydrocarbons; those formed from saturated hydrocarbons retain their present designation as *methyl*, *ethyl*, &c.; those from unsaturated hydrocarbons change the suffixes *-ene* and *-ine* into *-enyl* and *-inyl*; thus allyl becomes 2 *propenyl*; propenyl, 1 *propenyl*;[1] acetenyl, *ethinyl*; and propargyl, 2 *propinyl*, &c.

When side-chains are present in side-chains the suffix *-yl* is changed into the letter *o*: *metho*, *etho*, &c.

Some examples will illustrate these rules.

| *Old Nomenclature* | | *New Nomenclature* |
|---|---|---|
| Di-methyl-ethyl-methane (figs. 56, 57, p. 14) | = | 2 . methyl-butane |
| Tetra-methyl-methane (fig. 60, p. 14) | = | 2′ . 2 . di-methyl-propane |
| Iso-hexane (fig. 64, p. 15) | = | 2 . methyl-pentane |
| Methyl-di-ethyl-methane (fig. 66, p. 15) | = | 3 . methyl-pentane |
| Tetra-methyl-ethane (fig. 68, p. 16) | = | 2 . 3 . di-methyl-butane |
| Tri-methyl-ethyl-methane (fig. 70, p. 16) | = | 2′ . 2 . di-methyl-butane |
| Amylene (fig. 182, p. 35) | = | 1 . pentene |
| Iso-propyl-ethylene (figs. 188, 189, p. 36) | = | 2 . methyl 3 . butene (fig. 188) |
| *a*-methyl-ethyl-ethylene (fig. 190, p. 36) | = | 2 . pentene (fig. 82, p. 20) |
| *β*- ,, ,, (fig. 191, p. 36) | = | 2 . methyl 1 . butene |
| Tri-methyl-ethylene (fig. 192, p. 36) | = | 2 . methyl 2 . butene |
| Piperylene (fig. 200, p. 38) | = | 1 . 4 . pentdiene |
| Acetylene (fig. 206, p. 39) | = | ethine |
| Crotonylene (fig. 212, p. 39) | = | 2 . butine |
| Valerylene (fig. 215, p. 40) | = | 2 . pentine |
| Di-methyl-tetra-acetylene (fig. 222, p. 41) | = | 2 . 4 . 6 . 8 . decatetrine |
| Valylene (fig. 223, p. 41) | = | 3 . 1 . pentenine |
| Di-allylene (fig. 224, p. 41) | = | 5 . 1 . hexenine |

Although the suffixes *-ane*, *-ene*, *-ine* may suit French chemists, there are, from an English point of view, several well-founded objections to their adoption, and they will probably have to be modified. The German chemists are still using them in the form proposed by Hofmann as *-an*, *-en*, and *-in*.

The nomenclature of hydrocarbons with closed chain as proposed by the French committee met with so many objections that the discussion was postponed to a future opportunity.

---

[1] In order to distinguish propyl from iso-propyl, propenyl from iso-propenyl, &c., the rule of forming the longest possible chain must not be applied to side-chains: iso-propyl will then become *metho-ethyl*; iso-propenyl, *metho-ethenyl*, &c.

## Part II.

# DERIVATIVES OF HYDROCARBON

## Oxygen Compounds

### ALCOHOLS AND PHENOLS

# Derivatives of Hydrocarbons

All compounds hitherto considered were composed of carbon and hydrogen only; hence their name *hydrocarbons*.

Commencing with methane we have seen paraffins, olefines, acetylenes, cyclo-hydrocarbons, consecutively derived from this the least complex of hydrocarbons by the simple process of removing hydrogen-atoms in pairs.

As methane is, as it were, the foundation-stone of the hydrocarbons, so these in turn are the foundation upon which a wonderful fabric is built by introducing elements into the binding cement of these hydrocarbons.

The most important of these introductions are the elements chlorine, bromine, iodine, oxygen, sulphur, and nitrogen. We shall first consider

# The Oxygen Derivatives

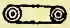
## Reaction of Hydrogen Peroxide upon Hydrocarbons

Oxygen: *Index*, *Chemical symbol*, O

The oxygen atom has two valencies, and combines therefore either with one dyad atom or with two monad atoms, or can satisfy two free valencies in a compound.

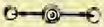
Like other atoms it cannot exist in the free state, but must combine, and, in the absence of anything better, will do so with a similar one forming a *molecule of oxygen*:

Fig. 313



Its combination with two hydrogen-atoms is *water*:

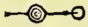
Fig. 314



Water

If we remove one hydrogen-atom from water we have a radical termed hydroxyl.

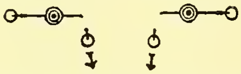
Fig. 315



Hydroxyl

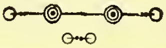
If we remove one hydrogen-atom from each of two water-molecules

Fig. 316



the hydroxyls, incapable of independent existence with their valencies free, unite forming a compound termed

Fig. 317



Peroxide of hydrogen, or a molecule of hydroxyl

Oxygen combines with all the other elements except fluorine. When the act of combining is accompanied by emission of heat and light it is called combustion. At the moment of combustion of hydrogen or hydrogen-compounds peroxide of hydrogen is always formed, and in all probability this precedes the formation of water invariably; but, at the same instant, the peroxide is reacted upon by hydrogen-atoms or other free valencies present (*Ch. N.* lx. p. 15; *Ber.* xviii. p. 1881), and there are, therefore, two incidences in combustion (oxidation) which may be illustrated thus:

One molecule of oxygen and one of hydrogen split up and form one molecule of peroxide of hydrogen.

Fig. 318

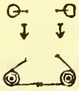


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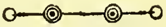
Fig. 319



Another molecule of hydrogen reacts upon the peroxide of hydrogen forming two molecules of water:

Fig. 320

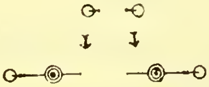


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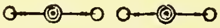
Fig. 321



If in the latter case one of the atoms in the hydrogen molecule is substituted by a hydrocarbon radical, the process will be the same, only we get one of the hydroxyls attached to a hydrocarbon radical instead of to a hydrogen-atom:

Fig. 322

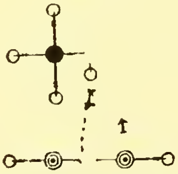


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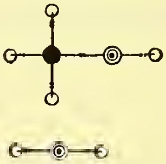
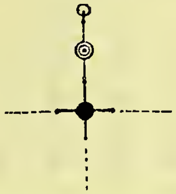
Fig. 323



In this way we can react upon all the hydrocarbons we have made acquaintance with in the preceding pages, introducing one or more hydroxyls into each. The class of compounds when thus formed from open chains is in the language of chemists called ALCOHOLS, and that from closed chains, PHENOLS.

Fig. 324



Alcohol's and phenol's *index*

## FIRST GROUP

## ALCOHOLS

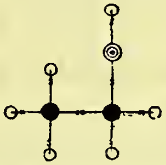
As there are numerous hydrocarbons, it follows that there must be many more alcohols, because not only can a varying number of hydroxyls be introduced into a molecule of hydrocarbon, but the same number may be placed in a variety of positions in that same hydrocarbon (isomers), their chemical behaviour characterising them as members of the same class.

The number and position of hydroxyls in the molecule are used as the readiest means of classification.

According to the *number* of hydroxyls, the alcohols are divided into classes, with one, two, three, &c., hydroxyls:

*a. Mon-acid alcohols* with one hydroxyl, *e.g.*

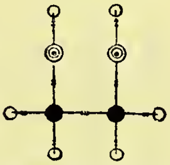
Fig. 325



Ordinary alcohol, spirits of wine; from ethane (fig. 16, p. 8)

*b. Di-acid alcohols* with two hydroxyls, *e.g.*

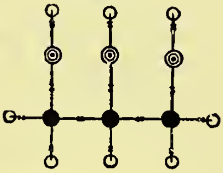
Fig. 326



Glycol, ethylene-alcohol; from ethane (fig. 16, p. 8) or ethylene (fig. 179 p. 35)

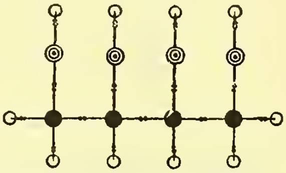
*c. Tri-acid alcohols* with three hydroxyls, *e.g.*

Fig. 327



Glycerol, glycerin; from propane (fig. 18, p. 8) *d. Tetra-acid alcohols* with four hydroxyls, *e.g.*

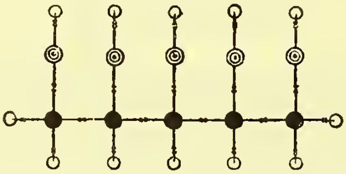
Fig. 328



Erythrol, erythrite; from butane (fig. 21, p. 9)

*e. Pent-acid alcohols* with five hydroxyls, *e.g.*

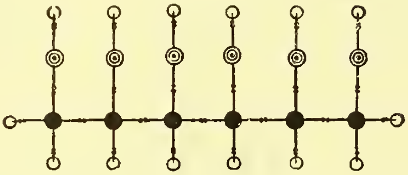
Fig. 329



Adonitol; from pentane (fig. 23, p. 9)

*f. Hex-acid alcohols* with six hydroxyls, *e.g.*

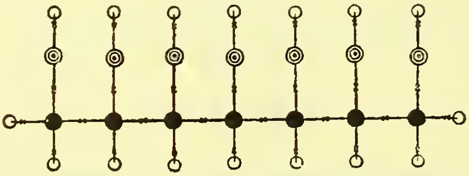
Fig. 330



Mannitol, mannite; from hexane (fig. 45, p. 12)

*g. Hept-acid alcohols* with seven hydroxyls, *e.g.*

Fig. 331



Perseïtol; from heptane (fig. 46, p. 12)

Oct-acid alcohols, mannoctite and glucooctite and also a non-acid alcohol glucononite have recently been prepared (*Ann.* cclxx. pp. 98–107; *Ber.* xxiii. p. 2235).

These classes are also termed mon-atomic, di-atomic, &c.; as, however, mon-acid &c. conveys a definite meaning which the other does not, the latter designation is preferred by many. 'Atomic' and 'acid' in this combination are not expressions for identical ideas, as we shall see when we come to consider the acids, and should therefore not be confounded.

Each of the classes is, according to the *position* of hydroxyls, subdivided into three other classes.

1. *Primary alcohols*, in which the carbon-atom in the hydroxyl-link is in direct connection with no more than *one* other carbon-atom, thus:

Fig. 332

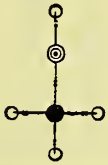
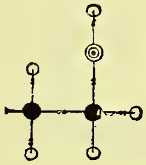
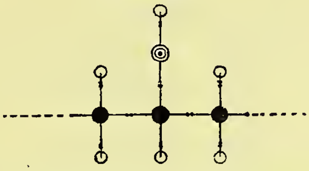


Fig. 333



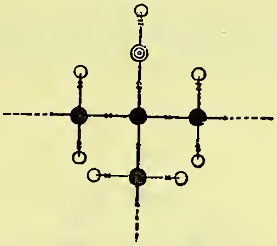
2. *Secondary alcohols*, in which the carbon-atom is in direct connection with *two* other carbon-atoms:

Fig. 334



3. *Tertiary alcohols*, in which the carbon-atom in the hydroxyl-link is in direct connection with *three* other carbon-atoms:

Fig. 335



The chemical behaviour of the three classes differs, and from their reactions conclusions may be drawn as to the positions of the hydroxyls.

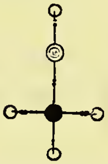
We shall now consider a few of the better known or more instructive members of the alcohol class.

## A. Mon-acid Alcohols

### 1. ALCOHOLS FROM PARAFFINS

From *methane* (fig. 14, p. 7) is derived methyl-alcohol or wood spirits:

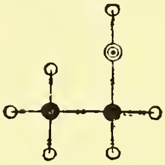
Fig. 336



Methyl-alcohol, carbinol, or wood spirits, $CH_4O$; b.p. 66°·8

From *ethane* (fig. 16, p. 8)

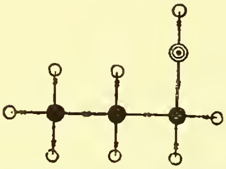
Fig. 337



Ethyl-alcohol, ordinary alcohol, spirits of wine, $C_2H_6O$; b.p. 78°·3

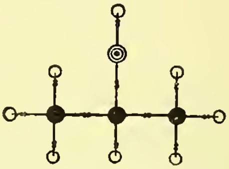
From *propane* (fig. 18, p. 8) two alcohols are derived, one primary and one secondary:

Fig. 338



Primary propyl-alcohol, $C_3H_8O$; b.p. 97°·4°;
occurs in raw spirit

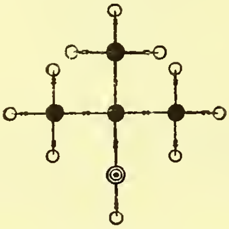
Fig. 339



Secondary propyl-alcohol, $C_3H_8O$;
b.p. 82°·8

From *butane* (fig. 21, p. 9) four alcohols are derived. They are all known, but only one of them has been introduced into materia medica, viz. tri-methyl-carbinol, derived from tri-methyl-methane (fig. 53, p. 13).

Fig. 340

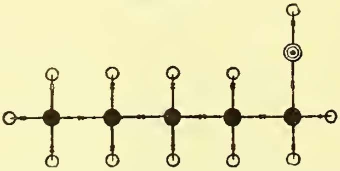


Tri-methyl-carbinol, $C_4H_{10}O$; m.p. 25°; tertiary alcohol; a sedative

From *normal pentane* and its two isomers, *iso-pentane* and *tetra-methyl-methane* (figs. 55, 57, 60, p. 14), eight different alcohols are possible, and all are now actually known. As they are rather instructive we shall give their pictorial representation here.

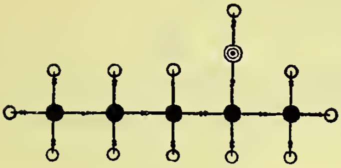
From the *normal pentane* three different alcohols may be derived, one primary and two secondary:

Fig. 341



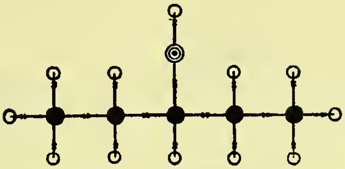
Normal amyl- (pentyl-) alcohol, $C_5H_{12}O$; b.p. 137°; primary alcohol; occurs in fusel oil

Fig. 342



Methyl-propyl-carbinol, $C_5H_{12}O$; b.p. 118°; secondary alcohol

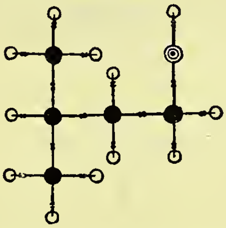
Fig. 343



Di-ethyl-carbinol, $C_5H_{12}O$; b.p. 116°·5; secondary alcohol

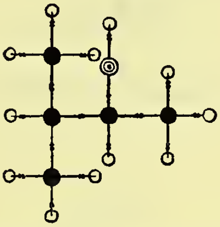
From *pseudo-pentane* (fig. 57, p. 14), four alcohols are possible and known:

Fig. 344



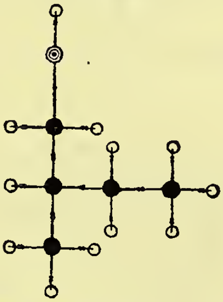
Iso-butyl-carbinol, inactive (iso-) amyl-alcohol, $C_5H_{12}O$; b.p. 131°; primary alcohol; chief constituent of fusel oil; poisonous; causes the toxic after-effects of intoxication by brandy

Fig. 345



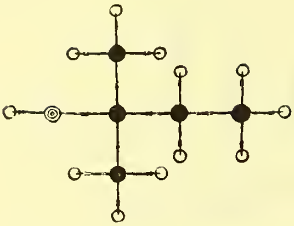
Methyl-iso-propyl-carbinol, $C_5H_{12}O$; b.p. 111–113°; secondary alcohol

Fig. 346



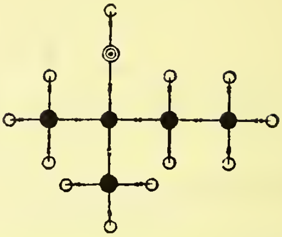
Active amyl-alcohol, $C_5H_{12}O$; b.p. 128°; primary alcohol; turns the plane of polarisation to the left

Fig. 347



or, hydroxyl changing position with one of the methyls at the end carbon:

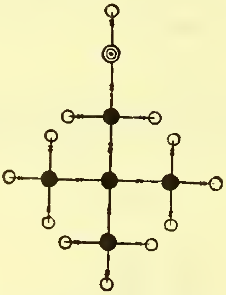
Fig. 348



Amylene-hydrate, di-methyl-ethyl-carbinol, $C_5H_{12}O$; b.p. 102°·5; tertiary alcohol; hypnotic, between paraldehyde and chloral

The eighth of possible pentyl-alcohols, according to our theory, has recently been prepared (*Ch. Ztg.* 1891, p. 15). Theoretically it is formed from tetra-methyl-methane, and its structure is thus illustrated:

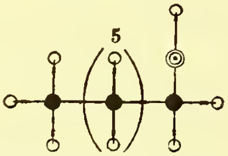
Fig. 349



Tetra-methyl-carbinol, $C_5H_{12}O$; m.p. 48-50°; primary alcohol

From *heptane* is derived

Fig. 350



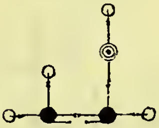
Primary heptyl-alcohol, $C_7H_{16}O$; b.p. 176°

Not much need be said about the rest of mon-acid paraffin alcohols. Cetyl alcohol or æthal, $C_{16}H_{34}O$, supposed to be a normal hexadecyl alcohol, is in combination with palmitic acid (as ether, *vide* p. 232), the chief constituent of spermaceti. All normal alcohols up to twelve atoms of carbon are known; but as to their isomers, theory and facts are sadly at variance. Out of 3,133 possible isomers, only sixty are known, and the more we might expect, the less there appear to be. The highest homologue is tarchonyl alcohol, $C_{50}H_{102}O$, but between this and dodecyl alcohol only eight alcohols are actually known out of eight to ten billions theoretically possible.

## 2. ALCOHOLS FROM OLEFINES

are formed in the same way as from paraffins, but comparatively few are actually known. The first member is formed from *ethylene* (fig. 179, p. 35):

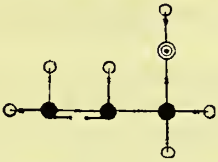
Fig. 351



Vinyl-alcohol, $C_2H_4O$; primary alcohol; occurs as an impurity in ether (*Ber.* xxii. p. 2863)

From *propylene* (fig. 180, p. 35) is derived

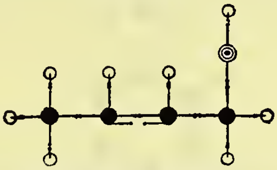
Fig. 352



Allyl-alcohol, propenyl-alcohol $C_3H_6O$; b.p. 96°·6; primary alcohol

From *pseudo-butylene* (fig. 185, p. 36)

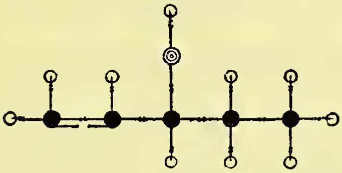
Fig. 353



Crotyl-alcohol, $C_4H_8O$; b.p. 117°; primary alcohol

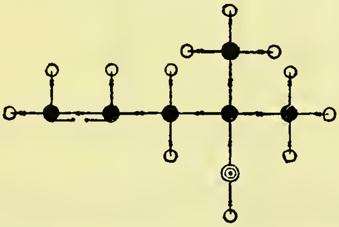
And as samples of secondary and tertiary alcohols:
From *normal amylene* (fig. 187, p. 36)

Fig. 354



Vinyl-ethyl-carbinol, $C_5H_{10}O$; b.p. 114° (*Beilst.* i. p. 261); secondary alcohol

Fig. 355



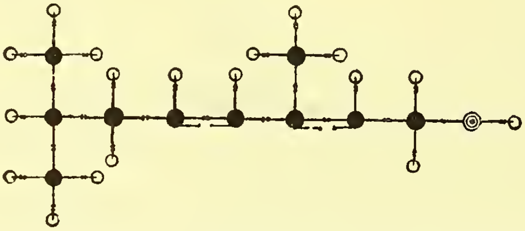
Di-methyl-allyl-carbinol; $C_6H_{12}O$; b.p. 119°·5; tertiary alcohol

## 3. ALCOHOLS FROM DI-ETHYLENES

A few alcohols belonging to this series are known.

From *di-methyl-butinyl-iso-propyl-methane* (fig. 140, p. 29) is derived

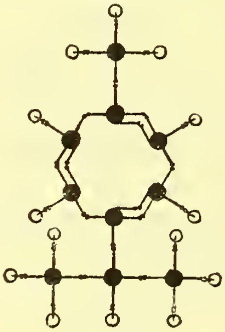
Fig. 356



Geraniol, $C_{10}H_{18}O$; b.p. 232°; primary alcohol; the fragrant fluid constituent (elæoptene) of Indian oil of geranium

When the hydroxyl and a hydrogen at the end of the chain and both hydrogen-atoms on the sixth carbon-atom (from the alcoholic end) are removed in form of water, $H_2O$, and $H_2$, the compound is transformed into *cymene,* with a closed chain (comp. figs. 140–142, p. 29).

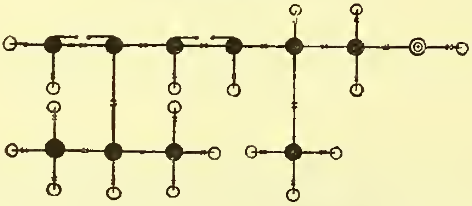
Fig. 357



Cymene

From *di-iso-propyl-butine* (fig. 143, p. 29) is derived

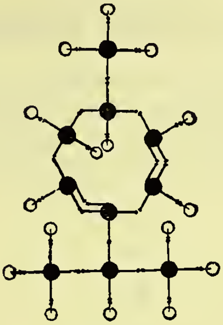
Fig. 358



Rhodinol, $C_{10}H_{18}O$; primary alcohol; elæoptene of attar of roses

When hydroxyl is removed from one end of the chain, and a hydrogen-atom from the other, the cyclo-hydrocarbon *limonene* is formed (comp. figs. 143, 144, p. 29).

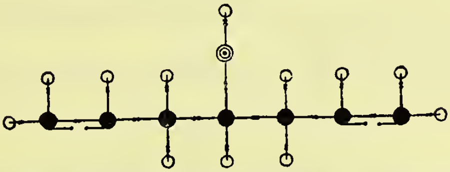
Fig. 359



Limonene

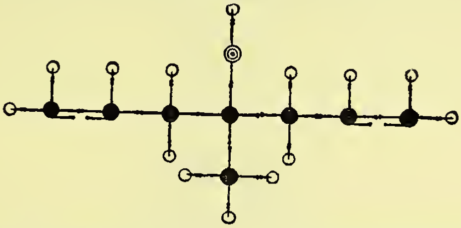
Instances of secondary and tertiary alcohols are

Fig. 360



Di-allyl-carbinol, $C_7H_{12}O$; b.p. 151°; secondary alcohol

Fig. 361



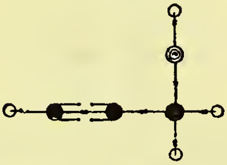
Methyl-di-allyl-carbinol, $C_8H_{14}O$; b.p. 158°·4; tertiary alcohol

No alcohols derived from tri- and tetra-ethylenes have been prepared.

## 4. ALCOHOLS FROM ACETYLENE

The only, as yet, actually known alcohol from the acetylene series is *propargyl-alcohol*; from *allylene* (fig. 207, p. 39)

Fig. 362

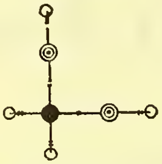


Propargyl-alcohol, $C_3H_4O$; b.p. 114°; primary alcohol

## B. Di-acid Alcohols

When two hydrogen-atoms in a hydrocarbon with open chain are substituted by hydroxyls, di-acid alcohols are formed. The two hydrogen-atoms must be from different carbon-atoms, because two hydroxyls cannot, as a rule, be joined to the same carbon-atom except when they are, as it were, counterbalanced by strong negative atoms joined either to the same or a neighbouring carbon-atom. For this reason a methylene-glycol

Fig. 363



Methylene-glycol; hypothetical

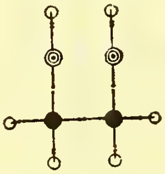
is not known to exist in free state, though there are compounds which must be regarded as its derivatives (*e.g.* methylal, fig. 481, p. 114).

As there are two hydroxyls in these compounds they are either di-primary, or primary-secondary, or di-secondary, &c.

### 1. ALCOHOLS FROM PARAFFINS: GLYCOLS

The first glycol must therefore be formed from *ethane* (fig. 16, p. 8)

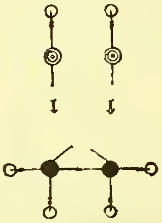
Fig. 364



Ethylene-glycol, $C_2H_6O_2$; b.p. 197°; di-primary alcohol

According to this representation the hydroxyls are joined to ethane by *substitution*. It may, however, be construed as an *addition* of hydroxyls to ethylene (fig. 179, p. 35);

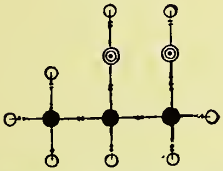
Fig. 365



and because it is prepared from compounds obtained in this way from ethylene it is termed *ethylene-glycol*, and all the other glycols similarly. The nomenclature in this case and in many others is singularly inconsistent and confusing. With the name of ethylene is connected the idea of a double bond; but such bond does not exist in ethylene-glycol, nor in any of the compounds from which it is directly prepared.

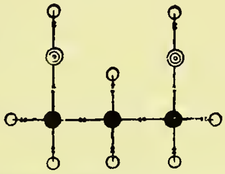
From *propane* are derived

FIG. 366



α-Propylene-glycol, $C_3H_8O_2$; b.p. 188°; primary-secondary alcohol

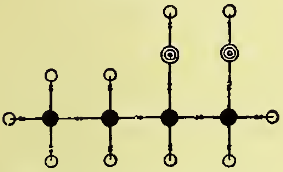
FIG. 367



β-Propylene-glycol, $C_3H_8O_2$; b.p. 216°; di-primary alcohol

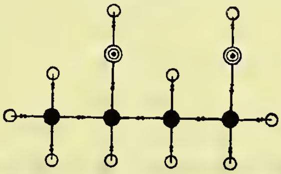
From *butane*:

FIG. 368



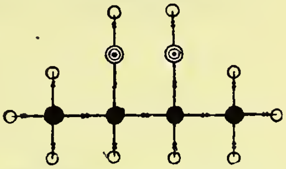
α-Butylene-glycol, $C_4H_{10}O_2$; b.p. 191°; primary-secondary alcohol

FIG. 369



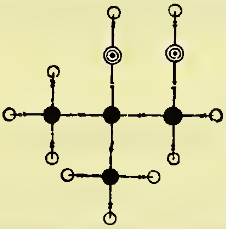
β-Butylene-glycol, $C_4H_{10}O_2$; b.p. 203°·5; primary-secondary alcohol

FIG. 370



Di-methyl-ethylene-glycol, $C_4H_{10}O_2$; b.p. 183°; di-secondary alcohol

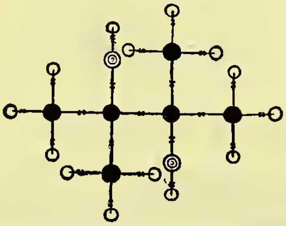
FIG. 371



Iso-butylene-glycol, $C_4H_{10}O_2$; b.p. 176°; primary-tertiary alcohol

Finally an instance of a di-tertiary glycol from *tetra-methyl-ethane* (fig. 68, p. 16), an isomer of hexane:

FIG. 372



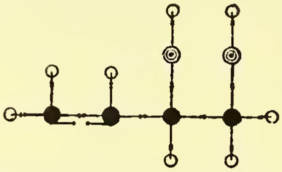
Pinacone, $C_6H_{14}O_2$; m.p. 35°; di-tertiary alcohol

All di-tertiary glycols are collectively termed pinacones from this compound.

### 2. ALCOHOLS FROM OLEFINES

From *butylene* (fig. 181, p. 35) is formed

Fig. 373

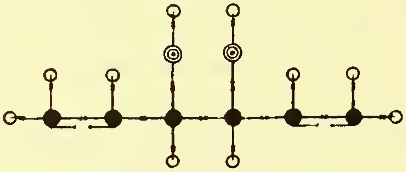


Butine-glycol, $C_4H_8O_2$; b.p. 199°; primary-secondary alcohol

### 3. ALCOHOLS FROM DI-ETHYLENES

From *di-allyl* (fig. 201, p. 38):

Fig. 374



Acro-pinacone, $C_6H_{10}O_2$; b.p. 160°; di-secondary alcohol

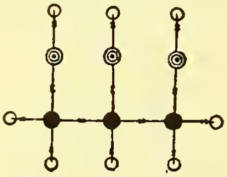
This compound is not a pinacone (di-tertiary glycol), in spite of its name.

Di-acid alcohols from other poly-ethylenes or acetylenes have not been prepared.

## C. Tri-acid Alcohols, or Glycerols

These alcohols are hydrocarbons in which three hydrogen-atoms have been replaced by hydroxyls. As only one of them can be placed on each carbon, the first alcohol we meet with must be formed from *propane* (fig. 18, p. 8):

Fig. 375



Glycerin, glycerol, $C_3H_8O_3$; m.p. 17–20°; b.p. 290°

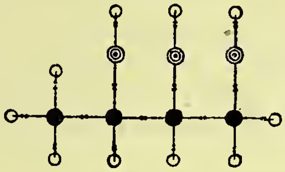
Glycerin has lately been used in treating hepatic cholic (*Ch. & D.* xli. p. 762).

It requires a temperature below −40° to solidify glycerin under ordinary circumstances; but the crystals, once formed, melt at 17–20°.

Under certain conditions, not exactly known (*e.g.* during transport), glycerin does not require so low a temperature to solidify.

A few only of this class are known, *e.g.*
From *butane* (fig. 21, p. 9):

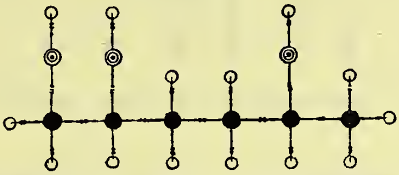
FIG. 376



Butyl-glycerin, $C_4H_{10}O_3$; b.p. under 27 mm. pressure, 172°

From *hexane* (fig. 62, p. 15):

FIG. 377



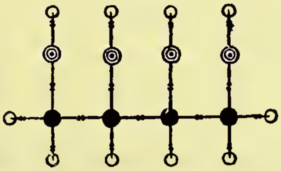
Hexyl-glycerin, $C_6H_{14}O_3$; b.p. under 10 mm. pressure, 181°

No tri-acid alcohol formed from ethylenes or acetylenes is known.

## D. Tetracid Alcohols, or Erythrols

Only one alcohol, formed from *butane* (fig. 21, p. 9), is known:

FIG. 378

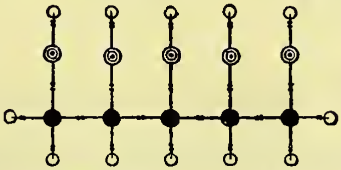


Erythrite, erythrol, $C_4H_{10}O_4$; m.p. 126°

## E. Pentacid Alcohols

Four alcohols are known, and are derived from pentane (fig. 23, p. 9):

FIG. 379



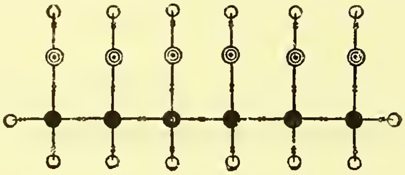
Adonitol, $C_5H_{12}O_5$; m.p. 102°

*Arabitol*, its isomer, is a laboratory product; *xylitol* and *rhamnitol*, likewise; *adonitol* was lately (*Ber.* xxvi. p. 633) discovered in *Adonis vernalis*; consequently the first pentacid found prepared by nature. The isomerisms of the three compounds are stereometrical (comp. p. 463), and the figure represents adonitol.

## F. Hexacid Alcohols

There are three alcohols found in nature: *mannitol* (three optical isomers), *dulcitol*, and *sorbitol.* They are all three formed from *normal hexane*:

Fig. 380



Mannitol, mannite, $C_6H_{14}O_6$; m.p. 166°

Their differences are stereometrical.

Mannite is widely distributed in nature, and is found especially in the dried juice of the manna-ash (*Manna officinalis*), in celery, sugar cane, rye bread, &c. Dulcitol or dulcite occurs in manna of Madagascar, in varieties of *melampyrum*, *scrophularia*, *euonymus*, *rhinantus*, &c. Sorbitol or sorbite is found in mountain-ash berries and in the juice of pears, apples, and medlars.

The manna that came pouring down on the Israelites in the desert was not this mannite, but probably an edible lichen, *Sphærothallia esculenta* (*Beilst.* i. p. 286).

There are several isomers possible, *e.g.*:

Fig. 381

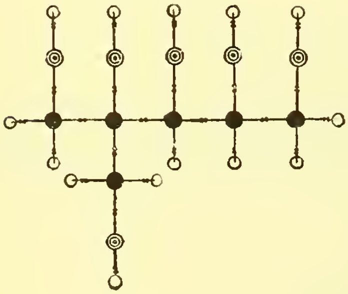


Fig. 382

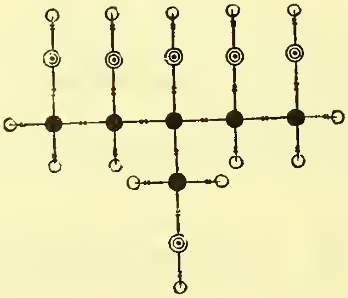
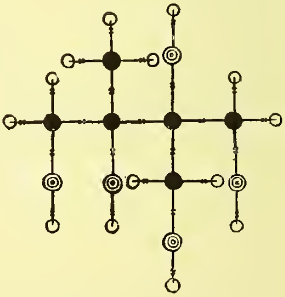


Fig. 383



Stereo-isomers of each are possible, but only the above mentioned are known.

## G. Heptacid Alcohols

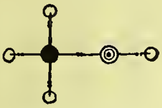
The only alcohols known are mannoheptitol or *perseïtol*, prepared from the fruits and leaves of *Laurus persea* (structure, *vide* fig. 331, p. 68), and glucoheptitol, a laboratory product.

# ALCOHOL RADICALS

When we remove that, for the alcohols, characteristic group, hydroxyl, compounds remain, most of which are identical with those obtained by removing hydrogen-atoms from hydrocarbons (*vide* p. 10), i.e. groups whose atoms have a sort of liking or affinity for each other, so that they will rather leave the rest of the compound than part company.

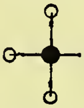
Thus we have by the removal of hydroxyl from

FIG. 384



Methyl-alcohol

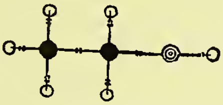
FIG. 385



Methyl

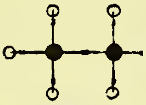
and from

FIG. 386



Ethyl-alcohol

FIG. 387



Ethyl

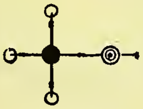
&c.

corresponding to those derived from hydrocarbons.

The mono-valent alcohol radicals are termed *alkyls*, and the di-valent *alkylenes*. The free valencies of the latter are of course distributed on *different* carbon-atoms, because two hydroxyls are never placed on the same carbon-atom in the free alcohols (as explained on p. 76). They are therefore different from the di-valent hydrocarbon radicals methylidene, ethylidene, &c. (p. 11), which have their two free valencies placed on *the same* carbon atom.

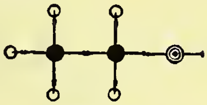
If we do not remove the whole of the hydroxyl, but only its hydrogen-atom, a group containing oxygen, and with one free valency, remains, *e.g.*

FIG. 388



Methoxyl

FIG. 389

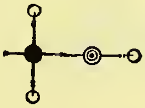


Ethoxyl

and are termed *methoxyl*, *ethoxyl*, &c., which, combined with other groups, is in nomenclature abbreviated to *methoxy-*, *ethoxy-*, &c.

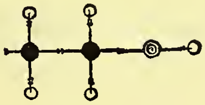
If, on the other hand, we remove a hydrogen-atom from the opposite end of the chain, the remainder is termed *hydroxy-* or *oxy-methyl*, *oxy-ethyl*, &c., or generally hydroxy- or oxy-alkyls, with one free valency (mono-valent radicals)

FIG. 390



Hydroxy-methyl

FIG. 391

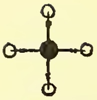


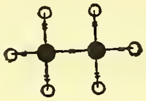
Hydroxy-ethyl

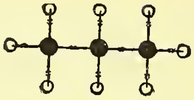
though the designation oxy-methyl is sometimes also used instead of methoxy &c.

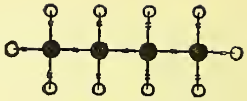
It is necessary, again, to impress on the mind that these are only theoretical experiments made

HYDRO-CARBONS


Methane, $CH_4$


Ethane, $C_2H_6$

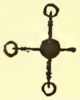

Propane, $C_3H_8$

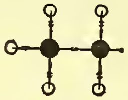

Butane, $C_4H_{10}$

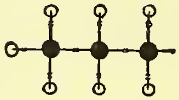
RADICALS

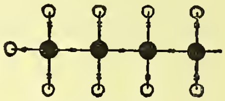
Alkyls

Mono-valent

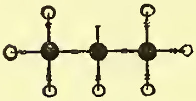

Methyl, $CH_3$

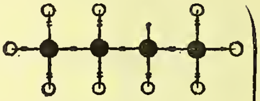

Ethyl, $C_2H_5$

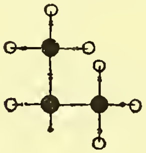

Propyl, $C_3H_7$

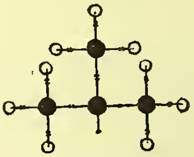

Butyl, $C_4H_9$

Isomers

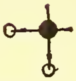

Iso-propyl, $C_3H_7$

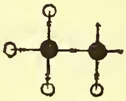

Iso-butyl, $C_4H_9$

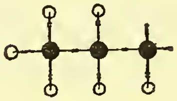

Iso-propyl, $C_3H_7$

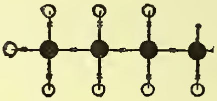

Iso-butyl, $C_4H_9$

Di-valent

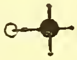

Methylene, methylidene, $CH_2$

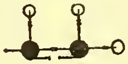

Ethylidene, $C_2H_4$

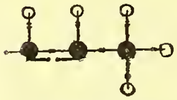

Propylidene, $C_3H_6$

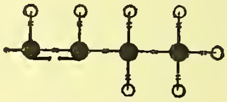

Butylidene, $C_4H_8$

Mono- and tri-valent


Methenyl, CH

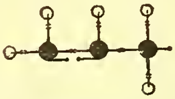

Ethenyl, vinyl, $C_2H_3$

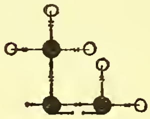

Propenyl, $C_3H_5$

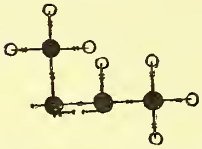

Crotonyl, $C_4H_7$

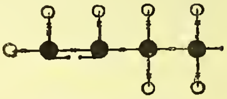
When the three free valencies are without double binding they are termed

Glyceryl Butenyl

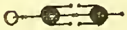

Allyl, $C_3H_5$

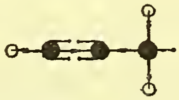

Iso-propenyl, $C_3H_5$


Iso-crotonyl, $C_4H_7$ and with the free valencies on different carbons, iso-butenyl


Butylenyl, $C_4H_7$

Mono- and penta-valent


Acetenyl, $C_2H$


Propinyl or propargyl, $C_3H_3$

for the sake of convenience. Such radicals do not and cannot exist in the free state with their unengaged valencies, nor can we practically introduce, for instance, methoxyl or ethoxyl by exchange into other compounds by abstracting water (*vide* p. 113) unless where a hydroxyl pre-exists. But *theoretically* we can do many things that at present are *practically* impossible. Thus, for the sake of showing the development of one compound from another, it is very convenient to say that we introduce a methoxyl or ethoxyl, when the intermediate compound containing the needed hydroxyl is only theoretically, not actually, known. It avoids the necessity of representing a hypothetical intermediate product that as yet exists only in imagination; for example, when we say that we introduce a meta-methoxyl into anol (fig. 446, p. 100), in order to show the derivation of eugenol (fig. 502, p. 119), it must be understood that we skip the intermediate phenol with a hydroxyl in metaposition, because it is not actually known.

The opposite table presents a summary of most of the radicals from hydrocarbons and alcohols with which we have to be made acquainted; ethylene and its derivatives, though not radicals in the common meaning (as they are independent molecules known in the free state), are often spoken of as radicals on account of their double bonds, with which they can join two free valencies in other compounds without substitution; they are not specified here, having already been mentioned in full.

Hydroxyls may also enter the aliphatic hydrocarbons in their combination with cyclo-hydrocarbons.

According to the number and position of hydroxyls the alcohols are classified just as before in mon-acid, di-acid, &c., and each again into primary, secondary, and tertiary alcohols (*vide* pp. 67–69). We will give the structures of some, enumerating them in the same order as we described the hydrocarbons (*vide* pp. 24 &c. and 42 &c.).

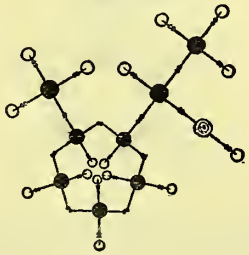
## Alcohols from Combined Aliphatic and Cyclo-hydrocarbons

Alcohols from combinations of tri- and tetra-methylene have not yet been prepared, though some derivatives of such alcohols, viz. aldehydes and acids, are known.

### I. ALCOHOLS FROM PENTA-METHYLENE'S COMBINATION WITH PARAFFINS

One alcohol is known from penta-methylene's (*vide* fig. 122, p. 26) combination with methane and ethane:

Fig. 392

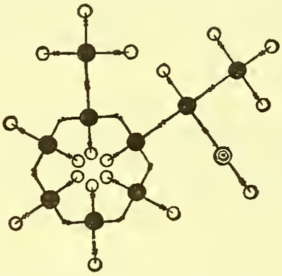


Methyl-penta-methylene-methyl-carbinol, $C_8H_{16}O$; b.p. 181°; mon-acid, secondary; has an odour like menthol

## II. ALCOHOLS FROM HEXA-METHYLENE'S COMBINATION WITH PARAFFINS

Ethane united to hexa-methylene (*vide* fig. 124, p. 26) together with methane forms an alcohol.

Fig. 393



Ortho-methyl-hexa-methylene-methyl-carbinol, $C_9H_{18}O$ ; b.p. 200° ; mon-acid, secondary ; menthol-like odour

Note the similarity in structure and physical properties between this and the preceding compound.

## III. BENZENE-ALCOHOLS

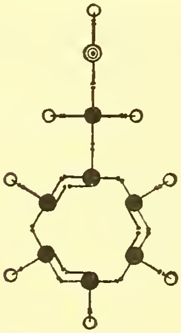
### A. Alcohols from Benzene's Combinations with Paraffins

#### 1. ONE BENZENE WITH ONE PARAFFIN

*a.* Mon-acid alcohols.

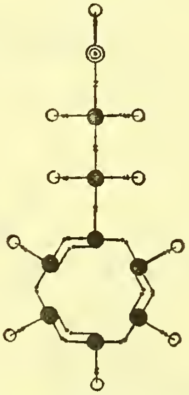
*Methane's*, *ethane's*, *propane's*, &c., combinations with *benzene* (*vide* figs. 232, 233, and 234, p. 44) form alcohols.

Fig. 394



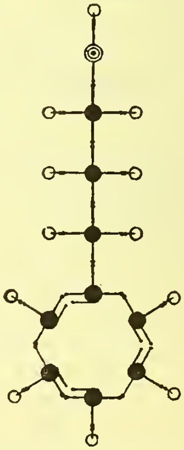
Benzyl-alcohol, $C_7H_8O$ ; b.p. 206°·5 ; mon-acid, primary (benzyl, *vide* fig. 175, p. 34)

Fig. 395



Primary styrolyl-alcohol, benzyl-carbinol, $C_8H_{10}O$ ; b.p. 212° ; mon-acid, primary

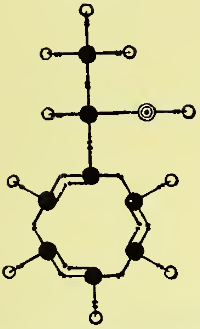
Fig. 396



Phenyl-propyl-alcohol, $C_9H_{12}O$ ; b.p. 235° ; mon-acid, primary

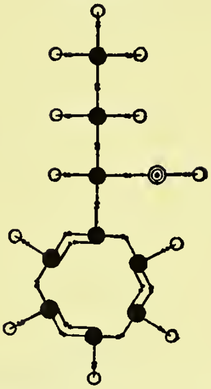
Isomers.

Fig. 397



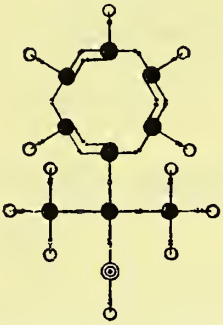
Secondary styrolyl-alcohol, methyl-phenyl-carbinol, $C_8H_{10}O$ ; b.p. 202° ; mon-acid, secondary

Fig. 398



Ethyl-phenyl-carbinol, $C_9H_{12}O$ ; b.p. 212° ; mon-acid, secondary

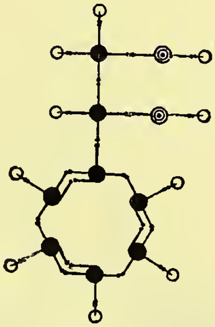
Fig. 399



Di-methyl-phenyl-carbinol, $C_9H_{12}O$ ; mon-acid, tertiary, hypoth.

## *b.* Di-acid alcohols.

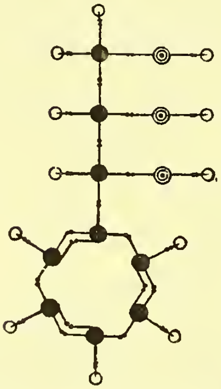
Fig. 400



Styrolene-alcohol, phenyl-glycol, $C_8H_{10}O_2$ ; m.p. 67° ; di-acid, primary secondary (*vide* fig. 233, p. 44)

### *c.* Tri-acid alcohols.

Fig. 401



Stycerol, phenyl-glycerol, $C_9H_{12}O_3$; gum-like mass; decomposes on heating; tri-acid, primary di-secondary (*vide* fig. 234, p. 44)

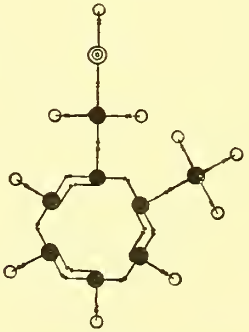
Tetra-, penta-, &c., acid alcohols are unknown.

## 2. ONE BENZENE WITH TWO PARAFFINS

### *a.* Mon-acid alcohols.

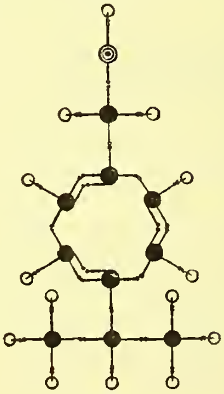
Instances of this sort of alcohols are

Fig. 402



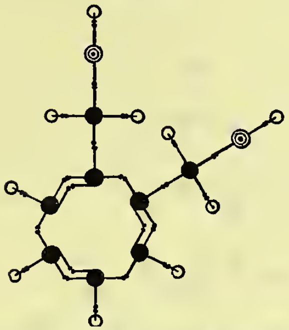
*o*-Tolyl-carbinol, $C_8H_{10}O$; m.p. 54°; mon-acid, primary; *m*- and *p*-compounds are also known (*vide* figs. 236, 237, 238, p. 44)

Fig. 403



*p*-Cumic-alcohol, $C_{10}H_{14}O$; b.p. 246°·6; mon-acid, primary (its hydrocarbon, cymene, *vide* fig. 240, p. 45) *b.* Di-acid alcohols.

Fig. 404

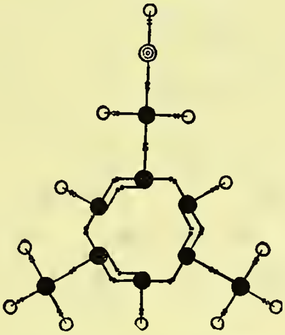


Ortho-position phtalyl-alcohol, $C_8H_{10}O_2$; m.p. 64°·5. Para-position tolylene-glycol, $C_8H_{10}O_2$; m.p. 112°. Di-acid, di-primary (*vide* figs. 236, 238, p. 44)

### 3. ONE BENZENE WITH THREE PARAFFINS

*a.* Mon-acid alcohols.
From *mesitylene* (fig. 242, p. 45)

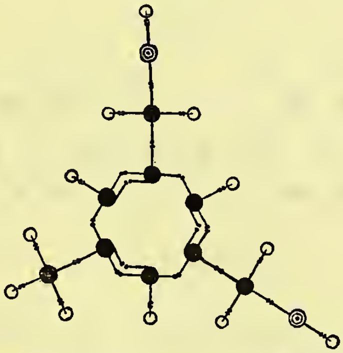
Fig. 405



Mesitylic alcohol, $C_9H_{12}O$; b.p. 220°; mon-acid, primary

*b.* Di-acid alcohols.
From *mesitylene* (fig. 242, p. 45)

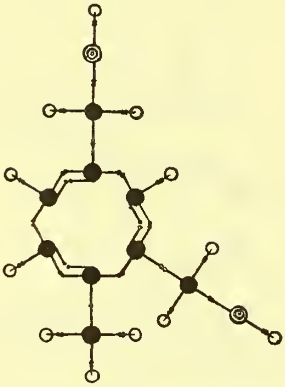
Fig. 406



Mesitene-alcohol, mesitylene-glycol, $C_9H_{12}O_2$; b.p. 190°, 20 mm. pressure; di-acid, di-primary

From *pseudo-cumene* (fig. 243, p. 45)

FIG. 407



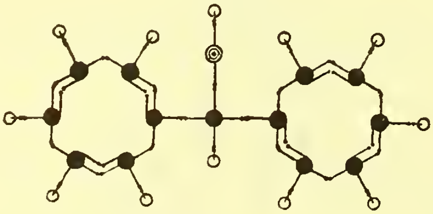
Pseudo-cumylene-alcohol, $C_9H_{12}O_2$; m.p. 77°·5 (97° 5 stereo-isomer ?); di-acid, di-primary

### 4. TWO BENZENES AND A PARAFFIN

*a.* Mon-acid alcohols.

From *di-phenyl-methane* (*vide* fig. 248, p. 46)

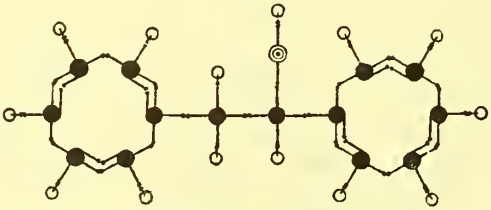
FIG. 408



Di-phenyl-carbinol, $C_{13}H_{12}O$; m.p. 68°; mon-acid, secondary

From *sym. di-phenyl-ethane* (*vide* fig. 250, p. 47)

FIG. 409



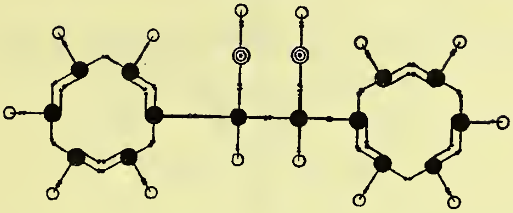
Toluylene-hydrate, phenyl-benzyl-carbinol, $C_{14}H_{14}O$; m.p. 42°; mon-acid, secondary

may also be considered a derivative of toluylene (fig. 255, p. 48) by addition of the elements of water; hence its name *toluylene-hydrate*.

*b.* Di-acid alcohols.

From *sym. di-phenyl-ethane* (*vide* fig. 250, p. 47)

Fig. 410

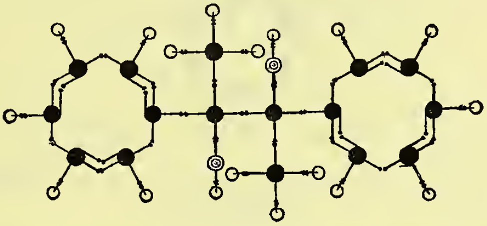


Hydrobenzoin, $C_{14}H_{14}O_2$; m.p. 134°; di-acid, di-secondary

An isomeric compound, *iso-hydrobenzoin,* which melts at 119°, also exists. Possibly it is an isomerism, which may be indicated by turning downwards one of the hydroxyls in the figure above. There are a great many similar (physical, in contradistinction to chemical) isomerisms, which will be explained later on (p. 463 &c.; comp. also p. 8).

From *di-phenyl-ethane* (fig. 250, p. 47)

Fig. 411



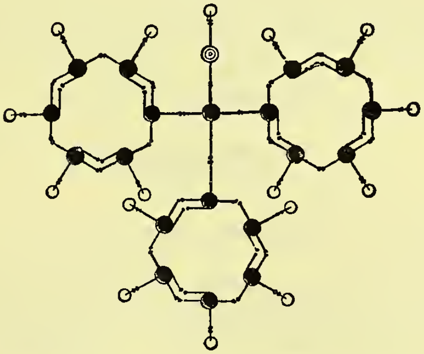
Aceto-phenone-pinacone, $C_{16}H_{18}O_2$; m.p. 120°; di-acid, di-tertiary

As to the name *pinacone* see p. 77. The compound may be regarded as pinacone in which two methyls are substituted by two phenyls.

### 5. THREE BENZENES AND A PARAFFIN

From *tri-phenyl-methane* (fig. 251, p. 47) is derived

Fig. 412

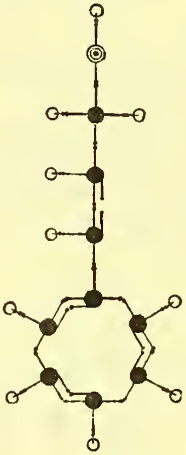


Tri-phenyl-carbinol, $C_{19}H_{16}O$; m.p. 159°; mon-acid, tertiary

## B. Alcohols from Benzene's Combinations with Olefines

A mon-acid alcohol is derived from *phenyl-propylene* (fig. 253, p. 47)

Fig. 413



Styrone, cinnamic alcohol, phenyl-allyl (propylene) alcohol, $C_9H_{10}O$ ; m.p. 33° ; mon-acid, primary occurs in storax

Alcohols belonging to this class have the general formula $C_nH_{2n-8}O$. Mention should therefore be made here of an alcohol that possesses such empirical formula, although its structure is not known (and yet chemists have been acquainted with it ever since the year 1788), viz. *cholesterin,* its homologues and isomers. It is widely spread in nature, occurs in blood, bile, brain, nerves, spleen, and generally in the cells of the living organism ; it is found in *cod-liver oil,* milk, eggs, &c. ; gall-stones consist almost entirely of it ; lanolin, or wool-fat, is almost exclusively cholesterins, either in the free state or as ethers united with stearic acid. It is a mon-acid alcohol, nearly related to the terpenes and camphors, perhaps also to the acids of the bile, glycocholic and taurocholic acid. From the molecular refraction the conclusion is drawn that there are four double bonds, and chemically it behaves like tertiary alcohols. The ultimate analysis and the determination of molecular weight (by Raoult's method) give numbers closely approximating those of $C_{26}H_{43}OH$ (*Monatsh.* xi. pp. 61–70).

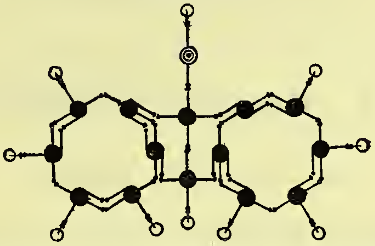
Isomers: *phytosterin* in seeds, and generally in the vegetable kingdom; *isocholesterin* in wool-fat; *paracholesterin* in a fungus; *caulosterin* in the yellow lupin; and *daucosterin* in carrots.

A higher homologue, $C_{27}H_{45}OH$ (*Monatsh.* ix. p. 421), and another, $C_{28}H_{47}OH$ (*J. Ch. Soc.* lviii. p. 757), have also been obtained.

Of the remaining alcohols formed from combinations of the aliphatic and cyclo-series there are but few, and no occasion for mentioning more than the following (two *benzenes* connected through *ethyl* by four of its valencies, or through two *methyls* by two valencies of each, in which case it may be considered three interlocked benzene rings).

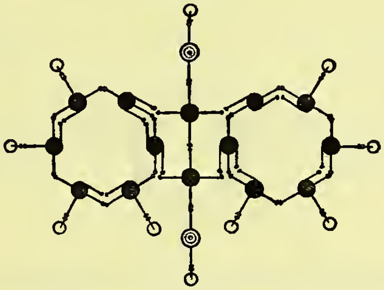
### C. Alcohols from Anthracene (fig. 307, p. 59)

Fig. 414



Anthranol, $C_{14}H_{10}O$; m.p. 163°, under decomposition; mon-acid, tertiary

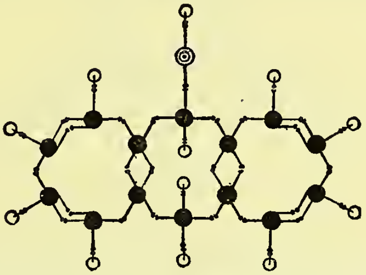
Fig. 415



Hydroxy-anthranol, $C_{14}H_{10}O_2$; m.p. not ascertained; di-acid, di-tertiary

From *anthracene di-hydrate*:

Fig. 416



Hydranthranol, $C_{14}H_{12}O$; m.p. 76°; mon-acid, secondary

## SECOND GROUP

# PHENOLS

When hydroxyl substitutes one or more hydrogen atoms *in the benzene-nucleus*, the resulting compounds behave in many ways differently from alcohols, and are therefore given a special name, phenols. They are allied to tertiary alcohols, as they behave like them towards oxygen, but differ from them in most of their other characteristic qualities. We will discuss the entering of hydroxyl into benzene and its derivatives, in the same order as the latter have been described before under Hydrocarbons.

As in the case of alcohols, they are classified according to the compounds they are derived from, each of which classes is subdivided into *mon-acid*, *di-acid*, &c., up to *hex-acid* phenols.

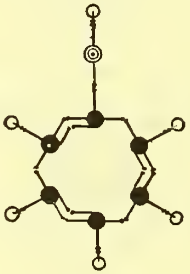
We commence, then, with replacing hydrogen by hydroxyl in benzene.

# I. Benzene-phenols

## A. Mon-acid Phenols

All hydrogens in benzene being of equal value, there can be but one member of this class:

Fig. 417



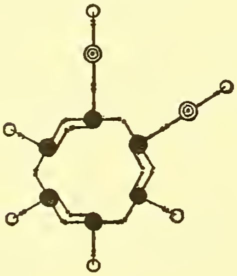
Phenol, carbolic acid, $C_6H_6O$; m.p. 41°; occurs in tars from wood, coal, &c.; is found in small quantities in the urine and castoreum; antiseptic

*Crude carbolic acid* contains scarcely any carbolic acid (*vide* p. 95).

## B. Di-acid Phenols

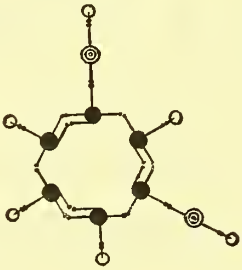
There are three phenols in this class according to the different positions of the hydroxyl: ortho-, meta-, and para-phenols.

Fig. 418



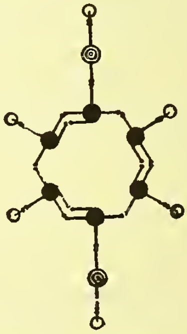
Pyrocatechin, catechol, ortho-dioxy-benzene, $C_6H_6O_2$; m.p. 104°; poisonous; used as a photographic developer

Fig. 419



Resorcin, meta-dioxy-benzene, $C_6H_6O_2$; m.p. 119°; powerful cauteriser, antiseptic, analgesic, and hæmostatic. Employed in the manufacture of fluoresceïn and eosin, two important dyes

Fig. 420

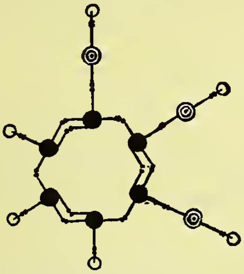


Hydroquinone, para-dioxy-benzene, $C_6H_6O_2$; m.p. 169°; rapid and delicate developer in photography; antipyretic and antiseptic

## C. Tri-acid Phenols

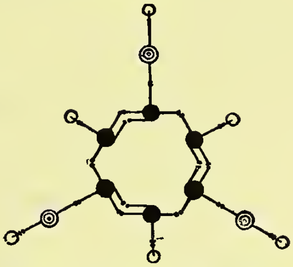
There are three of them corresponding to the positions 1 : 2 : 3 (vicinal, *vide* p. 43), 1 : 3 : 5 (symmetrical), and 1 : 3 : 4 (asymmetrical).

Fig. 421



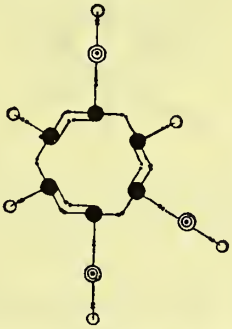
Pyrogallic acid, pyrogallol, $C_6H_6O_3$; m.p. 115°; antiseptic; very poisonous; absorbs oxygen powerfully; formerly much used in photography as a developer

Fig. 422



Phloroglucin (-ol), $C_6H_6O_3$; m.p. 217°; colours lignin red, and is therefore used as a test of wood-pulp in paper, also in medicine as an antiseptic and antipyretic

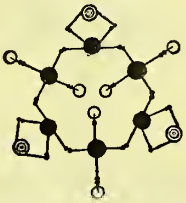
Fig. 423



Hydroxy-quinol, oxy-hydro-quinone, $C_6H_6O_3$; m.p. 140°

Phloroglucin seems capable of assuming two forms according to the character of the substance with which it comes in contact. The second form is a re-arrangement of the oxygen- and hydrogen-atoms, including the double bonds, and is represented thus:

Fig. 424

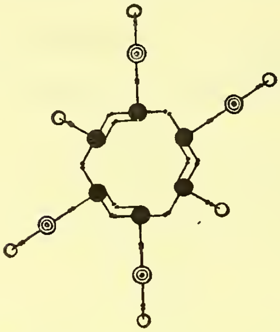


Desmotropic form of phloroglucin; contains three ketones (*vide* p. 138) instead of three hydroxyls

Such re-arrangement is termed *desmotropism* when a change in the bonds is involved; if not, it is termed *tautomerism*, which is, however, frequently used in both cases.

## D. Tetr-acid Phenols

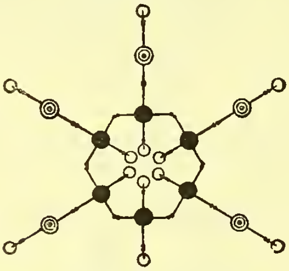
Fig. 425



Tetra-hydroxy-benzene, $C_6H_6O_4$; m.p. 148–220°

## E. Pent-acid Phenols

Fig. 426

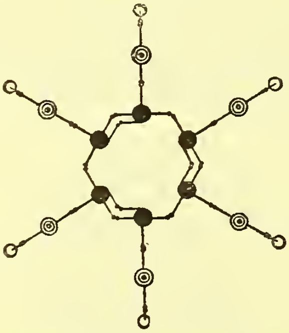


Quercite, $C_6H_{12}O_5$; m.p. 225°

derived from hydrated *benzene* (benzene-hexa-hydride, fig. 124, p. 26), and is, therefore, strictly not a phenol, but a *hydrated* phenol. Pinite seems to belong to this class, but the difference in structure is not sufficiently understood.

## F. Hex-acid Phenols

Fig. 427



Hexa-hydroxy-benzene, $C_6H_6O_6$; decomposes by heating without melting

Inosite, *phaseo-mannite*, *sennite*, *matezite*, *dambose*, $C_6H_{12}O_6$; m.p. 210°, is hexa-hydroxy-benzene-hexa-hydride, or quercite in which all six hydrogens have been replaced by hydroxyls. It is found in the muscles of the heart, in the lungs, the milt, the liver, the kidneys, the brain, and in the urine; also in plants.

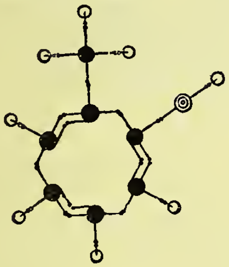
# II. Toluene-phenols

From *toluene* (fig. 232, p. 44) several important phenols are derived:

## A. Mon-acid Phenols

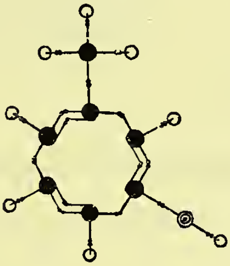
Three are possible:

Fig. 428



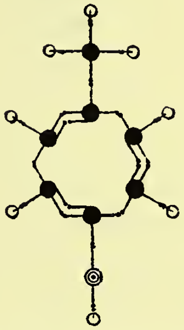
Ortho-cresol, $C_7H_8O$; m.p. 30°

Fig. 429



Meta-cresol, $C_7H_8O$; b.p. 203°

Fig. 430



Para-cresol, $C_7H_8O$; m.p. 36°

*o*- and *p*-Cresol is found in the urine of horses, *p*-cresol also in the human urine during some diseases. They are all found, together with carbolic acid, in coal-tar, from which they are produced by distillation.

The better sorts of what is called *crude carbolic acid* (soluble in a solution of caustic soda) contain scarcely any carbolic acid, but are mixtures of cresols, the carbolic acid having been already distilled off on account of its higher value.

The crude cresols are little used as such, because they are but slightly soluble in water, and have a higher specific gravity. There are in use the so-called 'carbolic lime' (crude cresols mixed with lime) and 'carbolic powder' (cresols mixed with clay).

On the other hand, after having been brought into a *soluble* form, they are largely employed as disinfectants.

## Modern Disinfectants

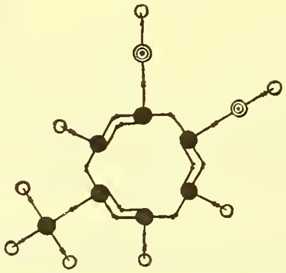
Of these there are a good many preparations that naturally divide themselves into two classes: 1, those which contain hydrocarbons and other tar compounds, and therefore form a milky fluid when mixed with water; and 2, those free from these admixtures, and which are therefore entirely soluble in water. Some of the preparations most in use are—

| | | |
|---|---|---|
| 1st class: | *Sapokarbol II, Little's Fluid, Jeyes' Disinfectant, Brockmann's Cresolin, Pearson's Creolin, Izal* | Mixtures of resinous soap with cresols, hydrocarbons, and pyridine-bases, originating from the coal-tar. The cresols remain dissolved in the dilute resinous soap, but the hydrocarbons separate and make the liquid milky |
| | *Artmann's Creolin* | Phenol sulphonic acid (fig. 1046, p. 292), in which the tar compounds are soluble, but are separated by diluting with water |
| | *Saprol* | Crude cresols and pyridine-bases mixed with hydrocarbons from petroleum factories, by which the sp. g. is lowered so much as to make the mixture float on water |
| 2nd class: | *Sapokarbol OO, Lysol, Pheneline* | Solution of cresols in soap free from tar compounds. |
| | *Solveol* | A concentrated solution of cresol, cresotic, or salicylic acid (fig. 823, p. 215) (fig. 838, p. 223) |
| | *Solutol* | A solution of cresols in sodium cresate (fig. 838, p. 223) |
| | *Kresin* | A solution of cresols in sodium cresoxyl-acetate (a combination of cresol and sodium-acetate) |
| | *Pixol* | Wood-tar dissolved in alkaline potash soap |

## B. Di-acid Toluene-phenols

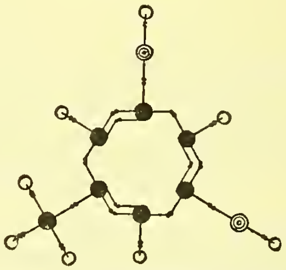
Six are possible, and four of them actually known. Only two need illustrating here.

Fig. 431



1:3:4. Homo-pyrocatechin, homo-catechol, $C_7H_8O_2$; m.p. 51°

Fig. 432



1:3:5. Orcin, orcinol, $C_7H_8O_2$; m.p. 108°

Asbolin, an alcoholic distillate from lampblack, recommended for tuberculosis, consists of pyrocatechin (fig. 418, p. 92) and homo-pyrocatechin (*Ph. C.* xxxiii. p. 527).

Orcin is prepared from the various species of variolaria (*Lichen orcina*), lecanora, and rocella, from which latter also archil (orseille) is prepared. From another variolaria (amongst other lichens) litmus is obtained.

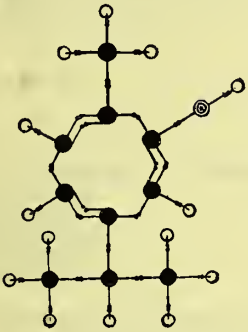
The two other phenols are 1:2:4 cresorcinol and 1:2:5 toluquinol or toluhydroquinone.

From *ethyl-benzene* (fig. 233, p. 44), *propyl-benzene* (fig. 234, p. 44), from *xylene* (figs. 236, 237, and 238, p. 44), *mesitylene* (fig. 242, p. 45), and *pseudo-cumene* (fig. 243, p. 45) diverse phenols are known but need not be considered, as their structures are analogous to the preceding ones, and none of them is of much importance. More interest to us have those which may be regarded as—

## III. Cymene- and Terpene-phenols

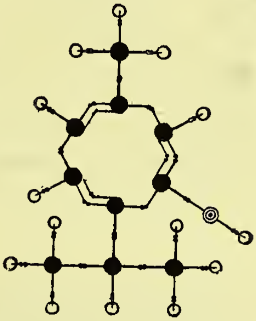
From *cymene* (fig. 240, p. 45) direct two phenols are derived:

Fig. 433



Carvacrol, ortho-cymophenol, $C_{10}H_{14}O$; b.p. 237°

Fig. 434



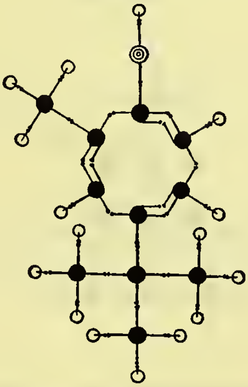
Thymol, meta-cymophenol, $C_{10}H_{14}O$; m.p. 50°

**Carvacrol** is found in *Thymus serpyllum, Satureja hortensis, Origanum hirsutum,* &c.; **thymol** in *Thymus serpyllum, Monarda punctata,* and *Carum-ajowan,* an Indian plant. Thymol has long been known to the Hindoos by the name of *Ajwan-ka-phyl.* Both carvacrol and thymol are antiseptics, more powerful than carbolic acid, and not poisonous. Used as antipyretics, and in rheumatism, typhus, whooping cough, bronchitis, &c.

**Antiseptin** (Radlauer) is a thymol preparation (a mixture of sulphate of zinc, iodide of zinc, thymol, and boric acid), *Ph. C.* xxxii. p. 500; *Ph. Ztg.* 1891, No. 63, p. 494.

From *methyl*-m-*iso-butyl benzene* (fig. 241, p. 45)

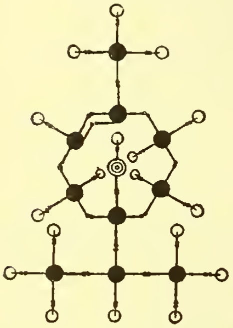
Fig. 435



Iso-butyl-*o*-cresol, $C_{11}H_{16}O$; b.p. 235°

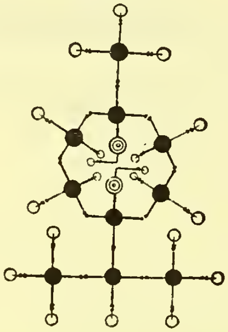
By hydrating (adding hydrogen-atoms to the double bonds inside) the benzene-ring, hydroxyls will form several important compounds

Fig. 436



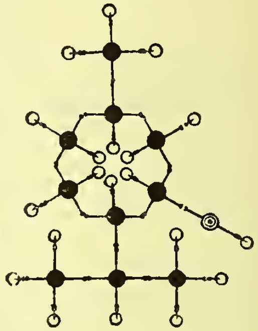
Terpineol, $C_{10}H_{18}O$; b.p. 215

Fig. 437



Terpine-hydrate, di-pentenylene-glycol, $C_{10}H_{20}O_2$; m.p. 116°

Fig. 438



Menthol, $C_{10}H_{20}O$ (? *Beilst*, iii. p. 260); m.p. 42°. Some authorities place hydroxyl in *o*-position to methyl; in the former case it is hexa-hydrated thymol, in the latter hexa-hydrated carvacrol

Terpineol is formed together with dipentene (*vide* p. 49) when oil of turpentine is boiled with sulphuric acid for the preparation of terebene. It has a pleasant smell of hyacinths.

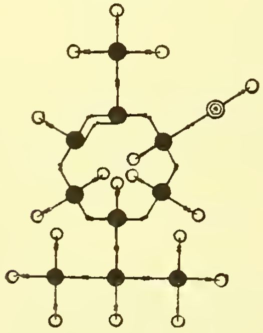
Terpine-hydrate, a di-acid phenol, is formed when a mixture of French or American oil of turpentine, alcohol, and nitric acid are allowed to stand for some days. Used as an expectorant.

Menthol occurs in oil of peppermint together with a terpene. It is employed as an anæsthetic and as a disinfectant. Formed into cones or pencils it is used externally for neuralgia and megrim, and internally for vomiting of pregnancy. Oil of peppermint containing but little terpene is solid at the ordinary temperature. Such oil comes from China and Japan, where it is known as Po-ho-yo.

Another compound, which must be looked upon as a derivative from cymene, is *Borneo camphor*, *borneol*, $C_{10}H_{18}O$; m.p. 206°.

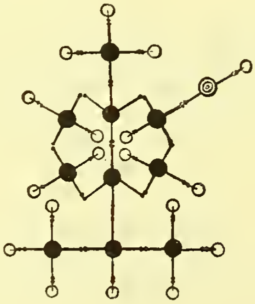
Its structure has been much discussed and is not yet settled; not any of the proposed constitutions explain in a satisfactory way all the reactions that camphor is capable of. I will give some of the structures proposed by different authors.

Fig. 439



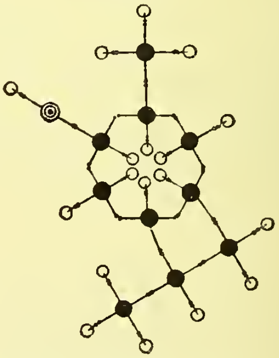
Beilst, iii. p. 262

Fig. 440



Roscoe and Schorlemmer, v. p. 428

Fig. 441



I. Norman Collie, *Ber.* xxv. p. 1114

Borneol, $C_{10}H_{18}O$; m.p. 206°; dextro-rotatory; a lævo-rotatory borneol is found in the rhizome of valerian

The first is Kekulé's benzene ring; the second is the diagonal bond, which symmetrically stretched out would be a di-tetra-methylene compound (*vide* p. 53); the third is a phenylene form binding the isopropyl (or rather propylene, fig. 180, p. 35) by two valencies.

Borneol, or Borneo camphor, occurs in the pith cavities of *Dryobalanops camphora*, a tree in Borneo. It can be prepared from ordinary camphor by heating an alcoholic solution with sodium, and is retransformed into ordinary camphor by the action of dilute nitric acid.

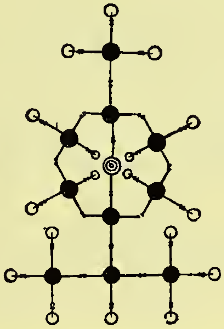
Borneol is said to act upon frogs and rabbits like curare.

There are two modifications, one dextro- the other lævo-rotatory.

An isomer is known: eucalyptol, one of the constituents of the oils of *eucalyptus*, *cajeput*, *rosemary*, and *wormseed* (*Semina cynæ*).

Eucalyptol is supposed to have this structure (*Ber.* xxiv. p. 1568).

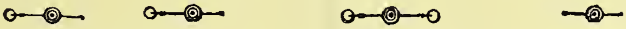
Fig. 442



Eucalyptol, cineol, cajeputol, $C_{10}H_{18}O$; b.p. 176°; antiseptic, antipyretic; externally for rheumatism, neuralgia, &c.

We meet here for the first time oxygen connecting two carbon-atoms, and how the oxygen-atom came into that position requires some explanation. If we look back upon terpine-hydrate (fig. 437, p. 98) we shall find two hydroxyls inside the ring (drawn a little irregularly for the sake of space); now when two hydroxyls, under favourable circumstances, come sufficiently near each other they have a strong inclination to form water.

Fig. 443



Two hydroxyls = water + oxygen

In the case of terpine-hydrate we have such an instance of favourable circumstances (and we will meet many more hereafter), where one of the hydroxyls passes away in the form of water, taking with it for that purpose a hydrogen-atom from the other hydroxyl, the oxygen-atom of which is left behind to comfort the bereaved carbon-atom by giving it the disengaged hand:

Fig. 444

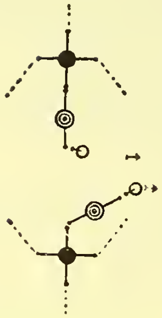
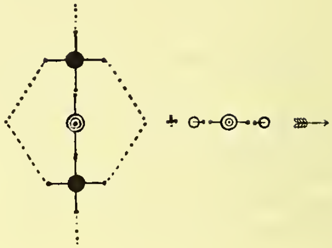


Fig. 445



Seen in this light we may look upon eucalyptol as formed from terpine-hydrate by removing a molecule of water.

Eucalyptol is one of the constituents of eucalyptus oil, which latter, however, must contain other and even more powerful germicides, because the vapour of eucalyptol takes twice as long to kill the bacilli of anthrax as the vapour of the oil itself does.

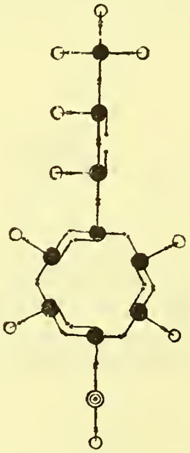
The influenza scare brought the eucalyptus oil well to the front, and as a consequence the market has been supplied with oil of the most varying quality, good, bad, and indifferent: there are about 150 varieties of the eucalyptus tree, some of which yield an oil unfit for medicinal use.

This oil is sometimes called *eucalyptol*, *eucalyptia*, or *eucalyptic extract*. Mixtures in which eucalyptus oil is a constituent, sometimes only to a small extent, have appeared in the market under the names of *eucalyptol*, *eucalyptol essence*, *sanitas eucalyptus oil*, and *eucalyptera*, while the name *eucalyptia* appears again, but this time as a hair-wash, *eucalyptine* and *eucalyptosine* as dentifrices (The *Med. Mag.* February 1893, p. 748).

## IV. Benzene-ethylene-phenols

There is but one phenol of this class to be mentioned derived from *phenyl-propylene* (fig. 253, p. 47):

Fig. 446



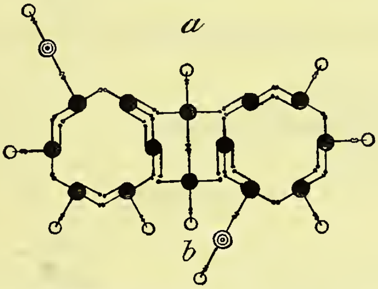
Anol, allyl-phenol, $C_9H_{10}O$; m.p. 93°; decomposes easily, even in an atmosphere of carbonic acid, when heated

Most text-books give this structure, according to which it is not allyl-phenol but propenyl-phenol (comp. figs. 253, 254, p. 47). *Beilst*, 1888, ii. p. 550, designates it as an allyl-phenol, and accordingly gives its structure thus: $HO-C_6H_4-CH_2-CH=CH_2$. *R. & S.* v. p. 196 also call it allyl-phenol. But according to its formation from *p*-methoxy-phenyl-crotonic (strictly methacrylic) acid through anethol (*vide* fig. 496, p. 117), its structure as represented above must be the correct one. The true allyl-phenol is not known at present, but several of its derivatives are, *e.g.* the methyl-ether, eugenol, and all its derivatives.

## V. Anthracene-phenols

From *anthracene* (fig. 307, p. 59) is derived a di-acid phenol:

Fig. 447



Rufol, β-di-hydroxy-anthracene, $C_{14}H_{10}O_2$; m.p. 197°

Both hydroxyls are here in *α*-position (comp. fig. 307, p. 59). When one is placed in *β*-position, the compound is called chrysazol, or *α*-di-hydroxy-anthracene; m.p. 184°. The designations of chrysazol as an *α*- and of rufol as a *β*-compound are rather misleading.

A question must force itself upon an attentive reader; even if we conclude from the elementary analysis that two oxygen-atoms are present, and that from the behaviour of the compound they are in the form of hydroxyls, how do we know their exact position in a molecule, which on account of its minuteness escapes our sight, though aided by the most powerful magnifying instruments?

The occasion being convenient, it can be explained in a manner not difficult to understand.

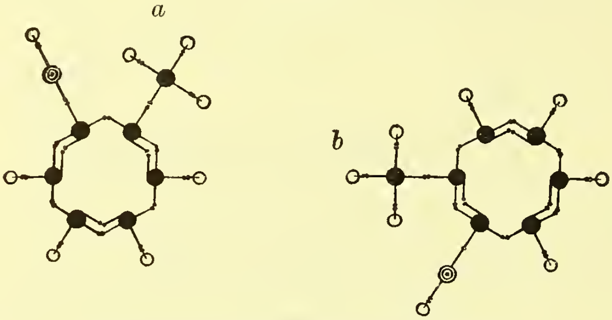
There are two ways, the synthetical and the analytical. The first is the best and most conclusive. We form the new compound by joining others whose structures are already well known. That is how we theoretically go along constructing interesting chemical bodies, exactly what we have been doing here all the time; but practically it is one of the most difficult tasks in chemistry, and those who discover new methods in this line become celebrities.

The other way is to split up the compound, and then having ascertained the products of the dismemberment we see if we can reconstruct the original compound by putting them together—on paper of course. This is the method always used in the first instance, and if it succeeds, the structure may be considered, sometimes, verified, in other cases most probable.

An illustrated example will make this easily understood. Suppose we have in some way or other obtained the compound rufol, we left just before this digression, and from its behaviour we conclude that we have before us an anthracene with two hydroxyls and wish to ascertain their position; then we split it up: it may be done by various processes, but by one of these we are able to divide it at one and the same time into two different compounds.

By the dismemberment about a moiety of the molecules will split up in such a way that the carbon-atom marked '*a*' will go with the left-hand benzene and '*b*' will go to the other. In the other moiety '*a*' will go to the right and '*b*' to the left. After providing all the *free* valencies thus created, with hydrogen-atoms, we obtain these two molecules:

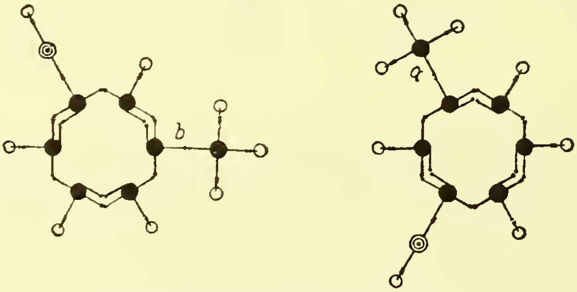
Fig. 449



Two molecules of ortho-cresol (fig. 428, p. 95)

and from the second way of division these molecules:

Fig. 450



Two molecules of meta-cresol (fig. 429, p. 95)

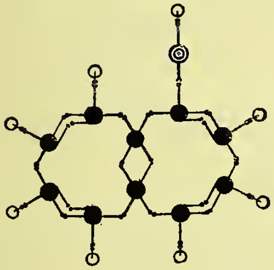
Both are easily distinguishable—one a solid, the other a liquid. No other position of the two hydroxyls could give these two compounds; consequently rufol must have the structure we have given it. I have adapted the actual investigations to suit our knowledge at this stage of the treatise. The conclusions as to the positions of the hydroxyls are actually drawn from researches on the action of caustic potash on anthrarufin (fig. 604, p. 147). Two different acids resulted from this action, viz. salicylic and meta-hydroxy-benzoic acid (pp. 215, 216). The structures of these two acids are represented by the two figures above 449, 450, when the methyls are exchanged for carboxyls. From the formation of these acids, and from the formation of anthrarufin, from *m*-hydroxy-benzoic acid we may with certainty conclude that the hydroxyls in anthrarufin are placed in *a*-position as represented in fig. 447, the reasoning being the same as set forth above; but anthrarufin is derived from rufol by transforming the two carbon-atoms, *a* and *b* into carbonyls; consequently the two hydroxyls in rufol must have the same position as in anthrarufin, i.e. *a*-positions.

# VI. Naphthalene-phenols, Naphthols

## A. Mon-acid Naphthols

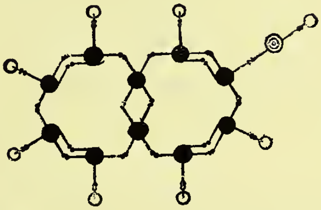
Three of the phenols derived from *naphthalene* (fig. 150, p. 31) are

FIG. 451



α-naphthol, $C_{10}H_8O$; m.p. 94°; antiseptic; is recommended as more powerful than β-naphthol, and seven hundred times less poisonous than mercuric bi-iodide

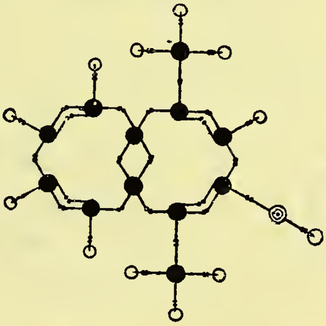
FIG. 452



β-naphthol, $C_{10}H_8O$; m.p. 122°; much used externally in skin diseases—eczema, psoriasis, scabies, &c. Internally toxic. The β-naphthol is always meant when the α-preparation is not expressly stated. A combination with bismuth (as phenolate) has been used with satisfactory results in cholera cases

Both are largely employed in the dye industry

FIG. 453

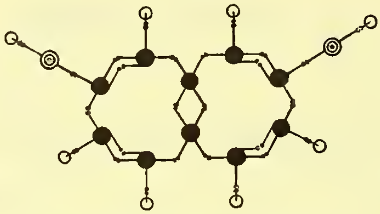


Di-methyl-naphthol, $C_{12}H_{12}O$; m.p 135°

### B. Di-acid Naphthols

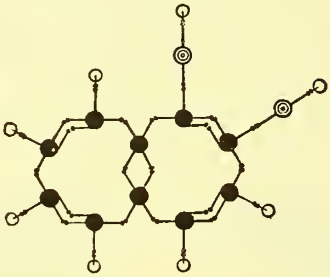
Ten di-acid naphthols differing in the positions of the two hydroxyls are theoretically possible and also known. The only ones to be specially mentioned are

Fig. 454



2 : 2′ (*vide* fig. 150, p. 31) di-hydroxy-naphthalene, $C_{10}H_8O_2$ ; m.p. 186° ; has been used in small doses as a roborant

Fig. 455

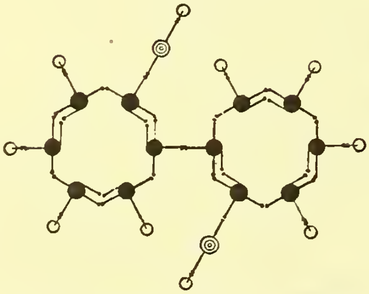


1 : 2-di-hydroxy-naphthalene, naphtho-quinol, $C_{10}H_8O_2$ ; m.p. 60°

## VII. Di-phenols

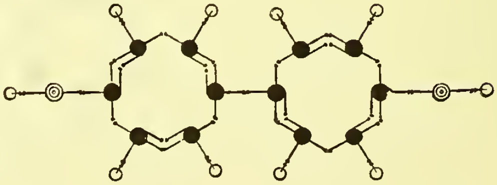
From *di-phenyl* (fig. 296, p. 57) several di-phenols are derived, with hydroxyls in different positions.

Fig. 456



α-(or *o*-) di-phenol, $C_{12}H_{10}O_2$ ; m.p. 123°

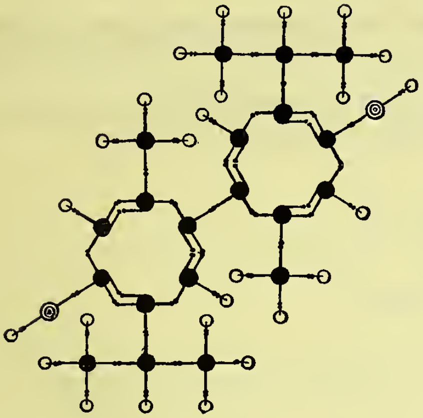
Fig. 457



γ-(*p*-) di-phenol, $C_{12}H_{10}O_2$ ; m.p. 270°

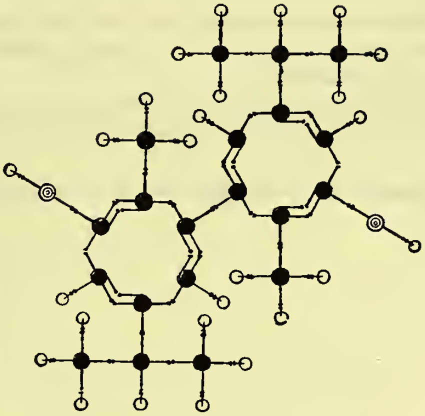
From *di-cymene* (fig. 297, p. 57) there are two isomers:

Fig. 458



Di-thymol, $C_{20}H_{26}O_2$; m.p. 165°

Fig. 459

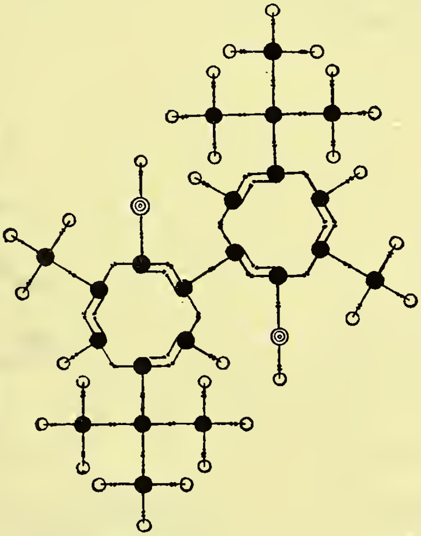


Di-carvacrol, $C_{20}H_{26}O_2$; m.p. 154°

From *di-methyl-di-*m-*isobutyl-di-benzene* (fig. 298, p. 57) a phenol is derivable, which has not yet been prepared; a further derivative (europhene, fig. 973, p. 270) is, however, known.

The structure of the phenol, which we will name europhenol to avoid a long systematical designation, would be

Fig. 460



Europhenol, $C_{22}H_{30}O_2$

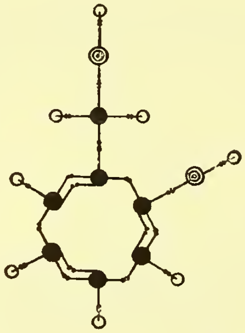
# VIII. Phenol-alcohols

When hydroxyls enter into both the benzene nucleus and its side-chains compounds are formed, which, at the same time, have the properties of a phenol and of an alcohol, and are therefore termed phenol-alcohols.

There are a great many derivatives from such compounds, but comparatively few of the phenol-alcohols themselves are actually known. It is sufficient to illustrate the undermentioned.

From *ortho-cresol* (fig. 428, p. 95) is derived

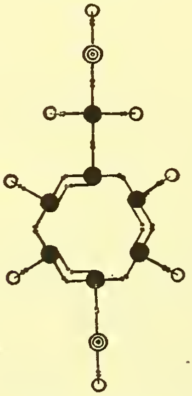
Fig. 461



**Saligenin, salicylic alcohol, ortho-hydroxy-benzyl alcohol, $C_7H_8O_2$; m.p. 82°; di-acid; is contained in a glucoside, salicin (fig. 635, p. 160)**

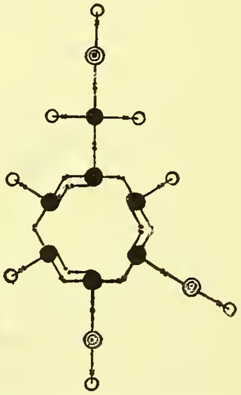
From *para-cresol* (fig. 430, p. 95)

Fig. 462



**Para-hydroxy-benzyl alcohol, $C_7H_8O_2$ m.p. 110°**

Fig. 463

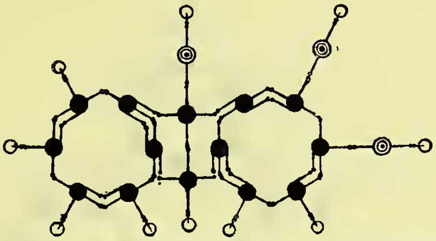


**Protocatechuic alcohol, di-hydroxy-benzyl alcohol; hypothetical is not yet prepared, but some derivatives (alcohol and aldehydes, fig. 561, p. 136, fig. 510, p. 123, figs. 562, 563, pp. 136, 137) are known**

## IX. Anthracene-phenol-alcohols

From *anthracene* (fig. 307, p. 59)

Fig. 464



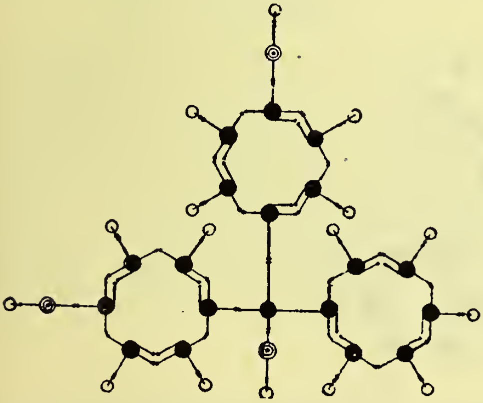
Anthrarobin, desoxy-alizarin, $C_{14}H_{10}O_3$; m.p. 208°; tri-acid; used in skin diseases as a substitute for chrysarobin and pyrogallol; not poisonous

Quinizarin-hydrate is a similar, but tetracid, compound with *two alcoholic* and two phenolic hydroxyls (1 : 4).

## X. Tri-phenol-alcohols

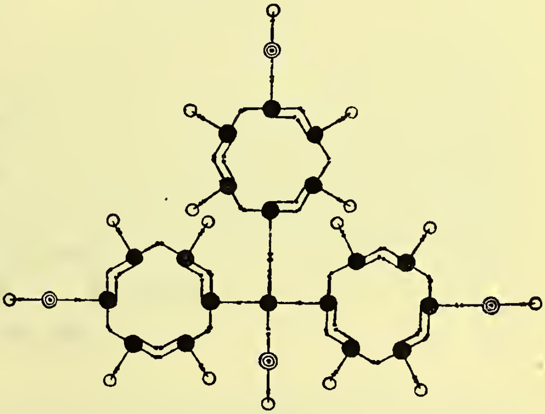
*Tri-phenyl-methane* (*vide* fig. 251, p. 47) or *tri-phenyl-carbinol* (fig. 412, p. 89) has a couple of phenol alcohols:

Fig. 465



Phenyl-di-phenol-carbinol, benzaurin, $C_{19}H_{16}O_3$; m.p. 100° red crystals

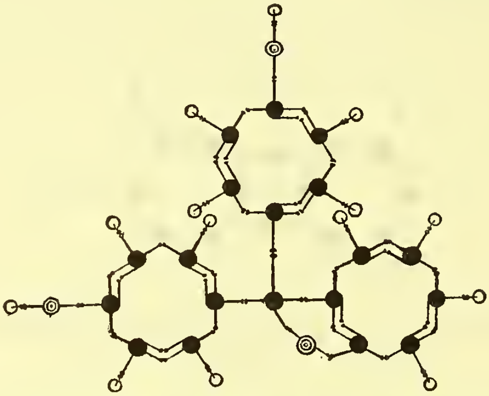
Fig. 466



Tri-phenol-carbinol, $C_{19}H_{16}O_4$

The latter compound is not stable, and has not been isolated because one of the para-hydroxyls will exchange places with one of the ortho-hydrogen atoms in order to get near enough to the methane-hydroxyl (intermolecular change; *vide* p. 40). This performance accomplished, the two hydroxyls form water in the manner just described, and the result is a dye:

Fig. 467

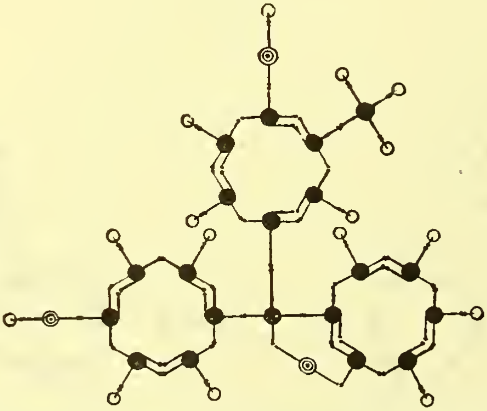


Aurin, $C_{19}H_{14}O_3$; m.p. above 220°; beautiful dark red crystals with a green metallic glance

That an intermolecular change must take place seems evident from the structure, the more so as it is generally admitted that a fully analogous process is performed in the formation of malachite-green (p. 360). Yet nearly all text-books teach that the oxygen-atom is in para-position, joining it to the valency in methane by a stroke of the pen.

If a methyl-group is placed in meta-position on the intermediate phenyl in the aurin-structure above, we get

Fig. 468



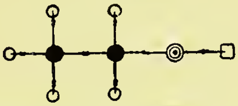
Rosolic acid, rosaurin, methyl-aurin, $C_{20}H_{16}O_3$; decomposes on heating above 270° without melting, ruby red crystals with metallic glance. Its alcoholic solution is turned red by the smallest trace of caustic soda, and is therefore a valuable indicator in alkalimetry

# ALCOHOLATES AND PHENOLATES

The hydrogen-atom in the hydroxyl of alcohols and phenols can be substituted by metals, and the above names are then conferred upon such compounds.

The only one at present of interest to us, besides one or two already mentioned, is

Fig. 469



Sodium-ethylate, Richardson's caustic, $C_2H_5ONa$; used for cauterising in lupus

The sign —□ represents a monad metal (in this case sodium), and —◇— means a dyad. The text will always indicate which metal is intended to be thus represented.

## Future Nomenclature

The alcohols are distinguished by suffixing the syllable *-ol* to the hydrocarbon from which it is derived. Two, three, or more hydroxyls are indicated by inserting *di-*, *tri-*, *tetra-*, &c., before the end syllable *-ol*, e.g.

| *Old Nomenclature* | | *New Nomenclature* |
|---|---|---|
| Methyl-alcohol (fig. 336, p. 69) | = | Methanol |
| Ethyl-alcohol (fig. 337, p. 70) | = | Ethanol |
| Glycerin (fig. 375, p. 78) | = | Propanetriol |
| Iso-butylene-glycol (fig. 371, p. 77) | = | 2 . Methyl- 1 : 2 propanediol |
| Acro-pinacone (fig. 374, p. 78) | = | 1 : 5 Hexdiene 3 : 4 diol |
| Mannite (fig. 380, p. 80) | = | Hexanehexol |

Cyclo-alcohols and phenols will have to wait until the nomenclature of their hydrocarbons has been settled.

Alcohol-radicals formed by the removal of hydroxyls are identical to corresponding hydrocarbon-radicals (p. 81) and receive their names as explained on p. 62; but those alcohol-radicals which have been formed by removing any other hydrogen than that of the hydroxyl receive the suffix *-ylol* added to the corresponding hydrocarbon's name: hydroxy-methyl becomes *methylol*; hydroxy-ethyl, *ethylol*, &c. The radicals formed by removal of the alcoholic hydroxyl's hydrogen (figs. 388 and 389, p. 81) will have to be looked upon as ether-formations (p. 124), and named accordingly: *methane-oxy*, *ethane-oxy*, &c., instead of metoxyl, ethoxyl, &c.

# PART III.

# Oxygen Compounds

## ETHERS

# Ethers

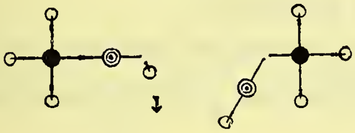
## A. Aliphatic Ethers

### 1. Ethers from Mon-acid Alcohols

Our first method of forming new compounds was to place two already known bodies side by side, and abstract a couple of hydrogen-atoms from them. The formation of paraffins in this way will be fresh in our memory (p. 8 *seq.*). In like manner we can, from alcohols, form new compounds; but now, when oxygen takes part in the operation, we abstract more than hydrogen—we draw water from them, and the result is an ether.

As a primary experiment we take the first alcohol we made by introducing a hydroxyl into methane, *methyl-alcohol* (fig. 336, p. 69), place two molecules side by side, and abstract water:

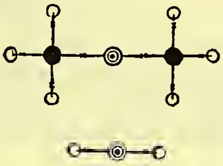
Fig. 470



Two molecules methyl-alcohol – water

=

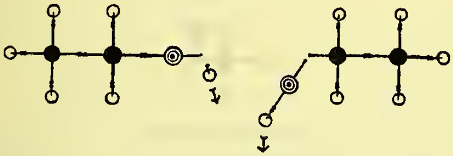
Fig. 471



One mol. methyl-ether, a gas (b.p. – 21°), and water, $H_2O$

or *ethyl alcohol*:

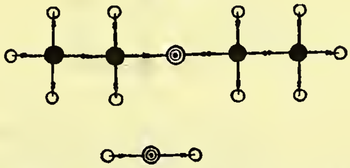
Fig. 472



Two molecules ethyl-alcohol — water

=

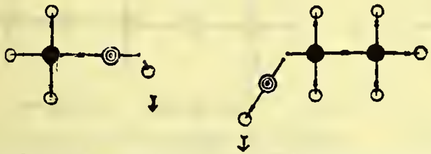
Fig. 473



One molecule ethyl-ether, sulphuric ether, or simply ether, $C_4H_{10}O$ (b.p. 34°·9), and water, $H_2O$

It is not necessary that the two molecules of alcohol should be of the same sort; we can take a molecule of methyl- and a molecule of ethyl-alcohol and perform the same operation.

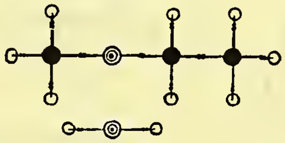
Fig. 474



One molecule methyl-alcohol + one molecule ethyl-alcohol

=

Fig. 475

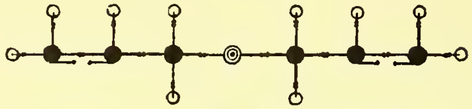


One molecule methyl-ethyl-ether, $C_3H_8O$ (b.p. 11°), used as an anæsthetic in lieu of chloroform

The former are termed simple ethers, the latter mixed ethers.

Simple and mixed ethers from unsaturated alcohols are also known, *e.g.* from *allyl-alcohol* (fig. 352, p. 73).

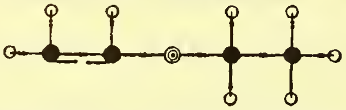
Fig. 476



Allyl-ether (a simple ether), $C_6H_{10}O$ ; b.p. 82°

and from *vinyl-* (fig. 351, p. 73) and *ethyl-alcohol*

Fig. 477



Vinyl-ethyl-ether (a mixed ether), $C_4H_8O$ ; b.p. 35°·5

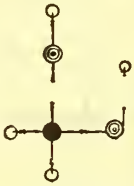
Theoretically we look upon an ether as an alcohol-radical joined to an oxygen-compound; thus we consider methyl-ether as composed of methyl and methoxyl (*vide* p. 81), and ethyl-ether as an ethyl joined to ethoxyl, &c. We do that, as already mentioned, for convenience' sake, because these oxy-groups frequently occur as if they were joined to an alcohol or phenol-radical.

## 2. Ethers from Di-acid Alcohols

Di-acid alcohols (*vide* p. 67) can also form ethers, and, having two hydroxyls, can form two series, according as one or both of them are joined to alcohols.

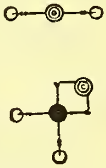
Methylene-glycol does not exist, for the reason, already set forth (p. 76), that two hydroxyls on the same carbon-atom will immediately form water.

Fig. 478



Methylene-glycol; hypothetical

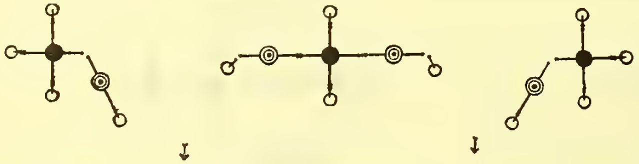
Fig. 479



Aldehyde and water

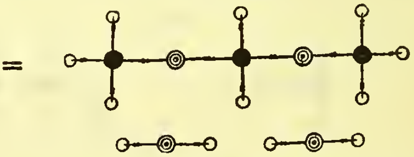
But if we could, at the moment when methylene-glycol should be formed, place two alcohols to take the two hydroxyls under treatment, like two policemen taking two brawlers in charge, two molecules of water would be separated, and the structure capable of existence.

Fig. 480



Methyl-alcohol Methylene-glycol Methyl-alcohol

Fig. 481

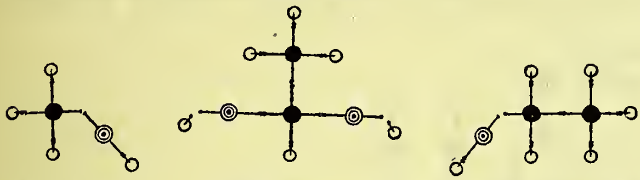


Methylene-di-methyl-ether (methylal), $C_3H_8O_2$ ; b.p. 42° ; hypnotic ; recommended in delirium tremens; for inhalation and subcutaneous injection; mixed with chloroform as an anæsthetic ; antidote to strychnine

In the same way is formed methylene-di-ethyl-ether, and also several ethylene-ethers, where the hydroxyls are not in combination with the same carbon-atom.

Alcohols from *ethylidene* (fig. 36, p. 11), where the hydroxyls are placed on the same carbon-atom, have not been prepared in the pure state; still it is not improbable that they exist in aqueous solution. Anyhow, ethers may be formed from them in the same fashion as they were formed from methylene glycol:

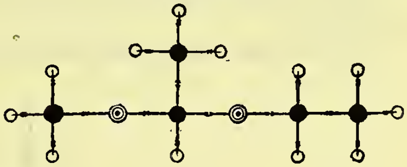
FIG. 482



Methyl-alcohol Ethylidene-glycol Ethyl-alcohol

=

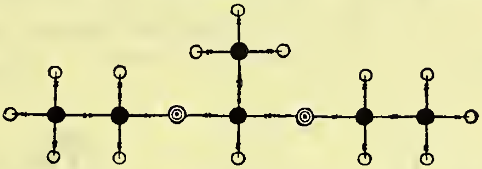
FIG. 483



Methyl-ethyl-acetal, $C_5H_{12}O_2$; b.p. 85°

Another is

FIG. 484



Acetal, di-ethyl-acetal, $C_6H_{14}O_2$; b.p. 104°; hypnotic

Ethers being alcohols from which water is abstracted, there is another formation (intramolecular) of ether from *glycol-alcohols*, *one* molecule of water being eliminated from *one* molecule of glycol.

FIG. 485

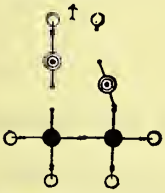


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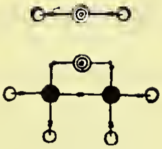
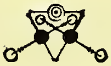
FIG. 486



or

FIG. 487



Ethylene-glycol (*vide* p. 76) = Ethylene-oxide, $C_2H_4O$; b.p. 13°·5

Compounds similarly constituted are termed alkylene-oxides.

This is a sort of intra-molecular ring formation, which is further developed when two molecules of ethylene-glycol join, in consequence of the separation of two molecules of water.

FIG. 488

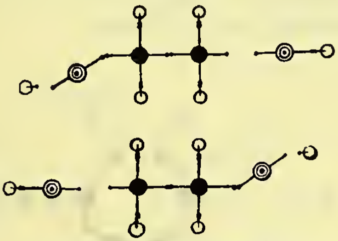


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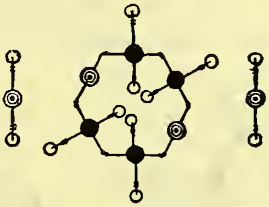
FIG. 489



Two molecules ethylene-glycol = Di-ethylene-oxide, $C_4H_8O_2$; b.p. 102°

Here is the first example of a cyclo-compound in which an oxygen-atom takes the place of a carbon-atom.

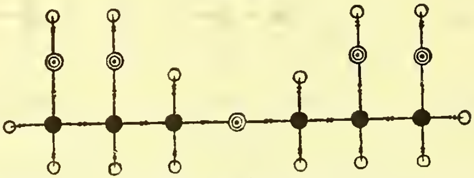
### 3. Ethers of Tri-acid Alcohols

Glycerin (fig. 375, p. 78) also forms ethers when joined by one, two, or three alcohols under elimination of water, as usual in ether formation, or by the joining of two molecules of glycerin; or, lastly, by elimination of water from one molecule, analogous to the formation of ethylene-oxide (*vide* figs. 486, 487).

The first sort of ether need not be illustrated, as it is merely a repetition of what we have just discussed.

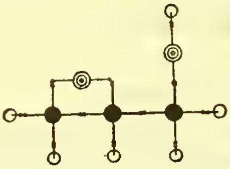
The two last ether-formations will appear thus:

Fig. 490



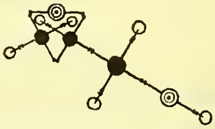
Di-glycerin, pyroglycerin (*Caution.*—By this name is generally understood nitro-glycerin), $C_6H_{14}O_5$ b.p. 220°, under 10 mm. pressure

Fig. 491



or

Fig. 492



Glycide-alcohol, $C_3H_6O_2$; b.p. 162°; unites the properties of ethylene oxide and an alcohol; its derivatives are termed glycides

## B. Cyclo-ethers

Phenols also form with their hydroxyls in this way compounds which must be considered ethers. According to the number of their hydroxyls they may be classified as—

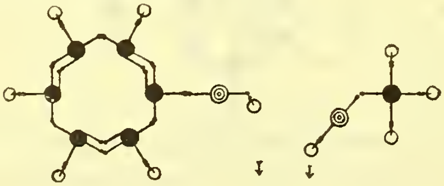
1. Phenyl-ethers, formed from mon-acid phenols and alcohols, or another phenol.
2. Phenol-ethers, formed from poly-acid phenols and alcohols, or phenols.
3. Phenyl-alcohol-ethers, when, in addition, an alcohol is present in phenyl-ethers.
4. Phenol-alcohol-ethers, when an alcohol is present in the phenol-ethers.

### 1. Phenyl-ethers

#### *a.* FORMED FROM MON-ACID PHENOLS AND ALCOHOLS

From *phenol* and *methyl-alcohol*:

Fig. 493

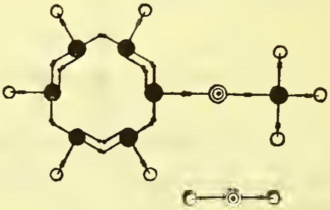


One molecule phenol

One molecule methyl-alcohol

=

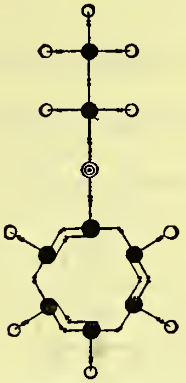
Fig. 494



One molecule anisol, anisoïl, methyl-phenyl-ether, methoxy-phenyl, $C_7H_8O$; b.p. 152°

From *phenol* and *ethyl-alcohol*:

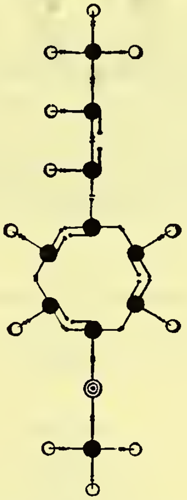
Fig. 495



Phenetol, phenetoïl, ethyl-phenyl-ether, ethoxy-phenyl, $C_8H_{10}O$; b.p. 172°

From *anol* (fig. 446, p. 100) and *methyl-alcohol*:

Fig. 496



Anethol, parallyl-anisoïl, $C_{10}H_{12}O$; m.p. 21°

occurs as the stearoptene of *oleum anisi* and *ol. fœniculi*, and is also one of the constituents of the essential oil of *Pimpinella anisum*. Is now much used in preference to oil of anise.

### *b.* FORMED FROM TWO MON-ACID PHENOLS

Fig. 497

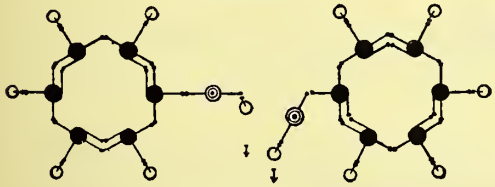


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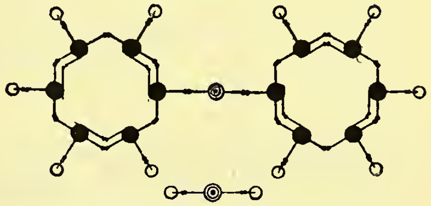
Fig. 498



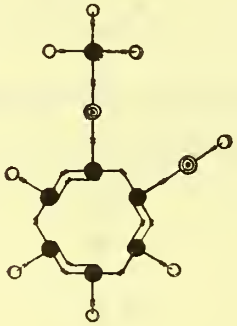
Two phenol-molecules = Phenyl-ether, $C_{12}H_{10}O$; m.p. 28°

## 2. Phenol-ethers

### *a.* FORMED FROM DI-ACID PHENOLS AND ALCOHOLS

From *catechol* (fig. 418, p. 92) and *methyl-alcohol*:

Fig. 499

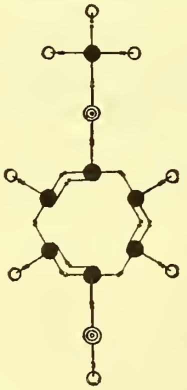


Guaiacol, catechol-mono-methyl-ether, $C_7H_8O_2$; when perfectly pure forms crystals; m.p. 28°·5; b.p. 205° (*Compt. Rend.* 116, p. 197); used in phthisis; relieves the cough, alleviates the expectoration, lessens the secretion, and improves the state of health generally, but is often not well borne by the stomach

*Commercial* guaiacol contains only about 35 per cent. of the pure compound; the rest is mostly phenol.

From *hydroquinone* (fig. 420, p. 92) and *methyl-alcohol*:

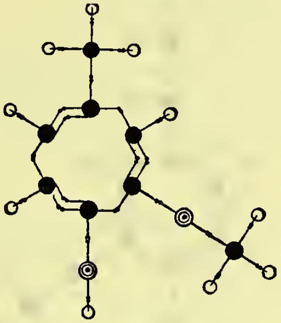
Fig. 500



Hydroquinone-methyl-ether, $C_7H_8O_2$; m.p. 53°

From *homo-pyrocatechin* (fig. 431, p. 96) and *methyl-alcohol*:

Fig. 501

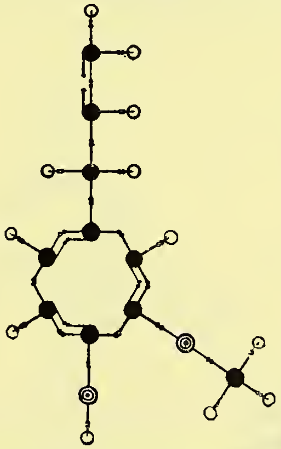


Creosol, homocatechol-mono-methyl-ether, $C_8H_{10}O_2$; b.p. 220°

Creasote, or creosote, distilled from wood-tar, is chiefly a mixture of guaiacol and creosol, while creosote from coal-tar is mainly phenol mixed with the three cresols (figs. 428–430, p. 95).

Further, from the hypothetical true *allyl-phenol* (p. 100) by introduction of methoxyl (the intermediate phenol, hydroxy-allyl-phenol with a hydroxyl in meta-position, is also unknown):

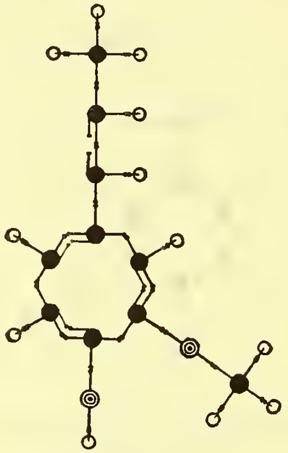
Fig. 502



Eugenol, $C_{10}H_{12}O_2$; b.p. 247°·5; is the chief constituent of oil of cloves, also found in many other oils; antiseptic and antipyretic, but inferior as a febrifuge

The double bond can be made to shift its place, the side-chain turning from an allyl (*vide* fig. 167, p. 33) into a propenyl radical (*vide* fig. 165, p. 33) by heating eugenol with an alcoholic solution of caustic potash.

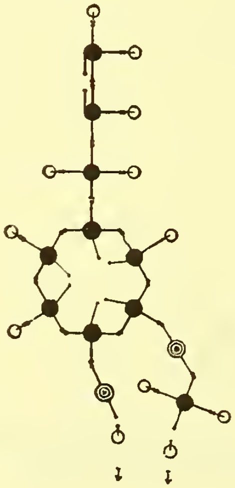
Fig. 503



Iso-eugenol, $C_{10}H_{12}O_2$ ; b.p. about 260° (*Ber.* xxiv. p. 2870) ; may also be considered a derivative of *anol* (fig. 446, p. 100) by introduction of a methoxyl in *p*-position ; it is extensively used in the preparation of artificial vanillin

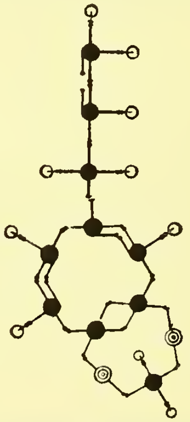
If we abstract two hydrogen-atoms from eugenol in this way (as to the re-arrangements of the double bonds, *vide* p. 54)

Fig. 504



we obtain

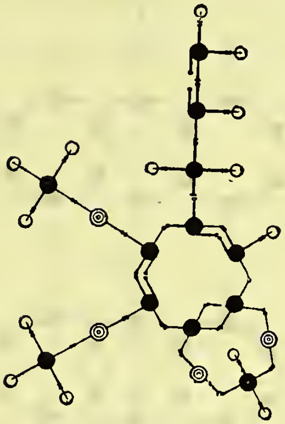
Fig. 505



Safrol, $C_{10}H_{10}O_2$ ; b.p. 232° ; the chief constituent (90 per cent.) of sassafras oil ; acts therapeutically like menthol

By introducing two methoxyls into this compound another constituent of ethereal oils is obtained :

Fig. 506



Apiol, $C_{12}H_{14}O_4$; m.p. 30°

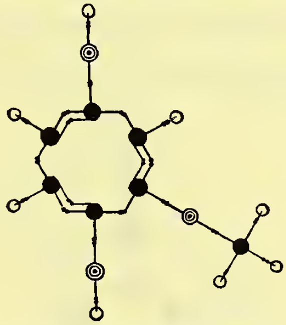
From the seeds of *Apium petroselinum.* Used in febris remittens and dysmenorrhœa. Should not be confounded with apiolum (*viride fluid. gallic.*), which is an alcoholic extract from the seeds.

Safrol and apiol are converted into *iso-compounds* (allyl into propenyl), analogous to eugenol, by heating with a solution of caustic potash.

### *b.* FORMED FROM TRI-ACID PHENOLS AND ALCOHOLS

From *(hydr)oxy-hydroquinone* (fig. 423, p. 93) and *methyl-alcohol*:

Fig. 507



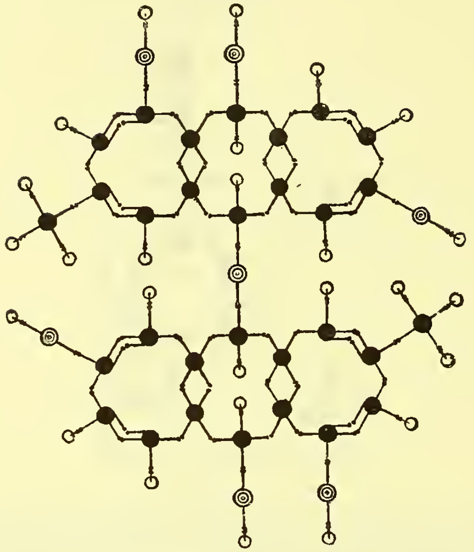
(Hydr)oxy-hydroquinone-methyl-ether, $C_7H_8O_3$

It has not been prepared yet, but the ethyl-ether and several derivatives have.

### *c.* FROM ANTHRACENE-PHENOL-ALCOHOL MUTUALLY

From the combination of two molecules of a *methylated* and *hydroxylated hydranthranol* (fig. 416, p. 91) is formed—

Fig. 508



Chrysarobin, $C_{30}H_{26}O_7$; m.p. 170°; yellow crystals

Valuable remedy for psoriasis, herpes tonsurans, eczema, &c. A parasiticide generally.

Commercial chrysarobin is the medullary matter of *Andira araroba,* and is also known as araroba, and Goa powder. Pure chrysarobin is extracted from the commercial product by benzene at boiling point.

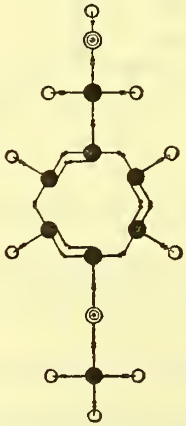
As regards the positions of hydroxyls and methyls see chrysophanic acid, p. 148

## 3. Phenyl-alcohol-ethers

FORMED FROM PHENOL-ETHERS (with one hydroxyl) AND ALCOHOLS

From *hydroquinone-methyl-ether* and *methyl-alcohol* (may also be regarded as derived from *para-hydroxy-benzyl-alcohol*) (fig. 462, p. 106):

Fig. 509



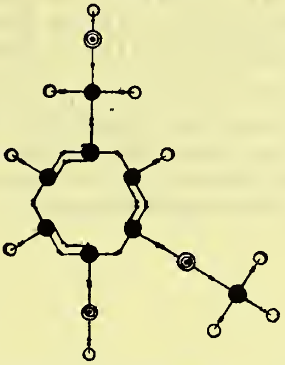
Anisic alcohol, para-hydroxy-benzyl-methyl-ether, $C_8H_{10}O_2$; m.p. 25°

## 4. Phenol-alcohol-ethers

FORMED FROM PHENOL-ETHERS (with more than one hydroxyl) AND ALCOHOLS

From *creosol* (fig. 501, p. 119) by converting methyl into *methyl alcohol,* or derivable from *homo-pyrocatechin* (fig. 431, p. 96):

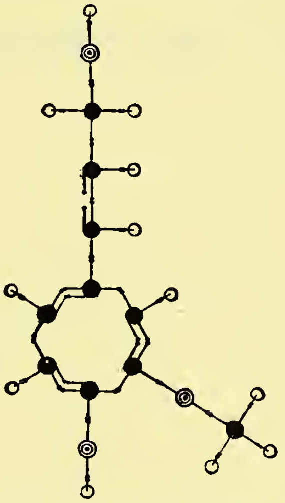
Fig. 510



Vanillic alcohol, $C_8H_{10}O_3$; m.p. 115°; by oxidation is formed vanillin, the substance that gives flavour and fragrance to vanilla (*vide* fig. 562, p. 136)

From *iso-eugenol* by converting propenyl into propenyl-alcohol (fig. 352, p. 73):

Fig. 511



Coniferyl-alcohol, $C_{10}H_{12}O_3$; m.p. 74°; occurs in the sap of coniferæ in combination with sugar as coniferin (a glucoside, *vide* fig. 636, p. 160), from which artificial vanillin is prepared (*vide* p. 137)

### Future Nomenclature

The proposed nomenclature of ethers is, to place '*oxy*' between the name of the two hydrocarbons connected through the oxygen, *e.g.*

| *Old Nomenclature* | | *New Nomenclature* |
|---|---|---|
| Methyl-ether (fig. 471, p. 113) | = | Methane-oxy-methane |
| Methyl-ethyl-ether (fig. 475, p. 113) | = | Ethane-oxy-methane |
| Vinyl-ethyl-ether (fig. 477, p. 114 | = | Ethane-oxy-ethene |

No rule informs us which hydrocarbon should take precedence; but in the example illustrating the nomenclature, the Congress has placed the longest chain first. What is to become of ethers from poly-acid alcohols is not stated, nor are we guided in the choice of a name for acetals, alkylene-oxides and glycides; perhaps they are included in *les composés à fonction complexes* on which a discussion *plus approfondie* is left to some coming Congress.

# Part IV.

## Oxygen-compounds

### ALDEHYDES AND KETONES

# Reaction of Hydrogen Peroxide upon Alcohols

## ALDEHYDES AND KETONES

### FORMATION

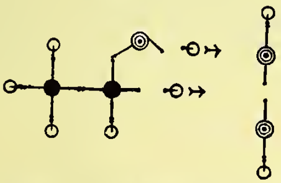
By the reaction of hydrogen-peroxide on hydrocarbons, alcohols were formed (p. 66); but its energy is not exhausted: it can react further on those same alcohols.

Though the operation is always the same, there is a difference in the result of its action according as the alcohol is a primary, secondary, or tertiary one (*vide* p. 69). From primary alcohols the resulting compound is termed an aldehyde; from secondary alcohols, ketones; and tertiary alcohols are split up into compounds of different composition, a ketone, and an acid, with, collectively, as many carbon-atoms as the original alcohol possessed altogether.

We will give an instance of each.

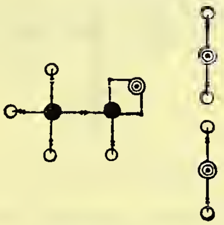
If we let hydrogen-peroxide react upon primary ethyl-alcohol (fig. 337, p. 70), its action may be thus illustrated:

Fig. 512



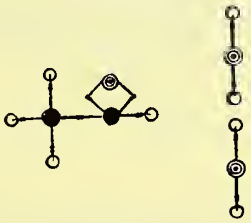
=

Fig. 513



or

Fig. 514

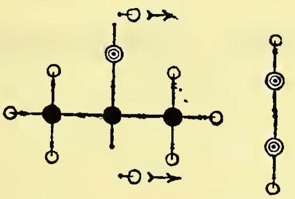


Ethyl-alcohol and hydrogen-peroxide = Aldehyde + water = Aldehyde + water

The difference in the drawing of the two aldehydes is merely the hydrogen-leg of the second carbon-atom in the last representation being stretched out in a horizontal direction; for several reasons it is generally more convenient so; but I shall sometimes have to use the first figure, too, in demonstrating the progress of sundry reactions.

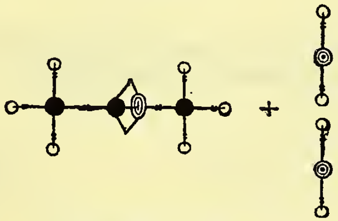
If we now take a secondary alcohol, *e.g.* secondary propyl-alcohol (fig. 339, p. 70), the reaction will take place in this way:

Fig. 515



Secondary propyl-alcohol + Hydrogen-peroxide

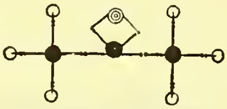
Fig. 516



Di-methyl-ketone + water

The illustration is a sort of perspective drawing, and in order to avoid that as much as possible I prefer representing the oxygen-atom in a position analogous to that of aldehyde, consequently thus:

Fig. 517



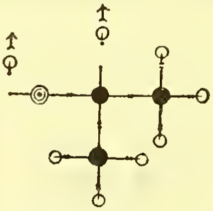
Di-methyl-ketone

This is perfectly justifiable, and a little consideration will show that it is in thorough accord with our theory.

We have already several times (*vide* p. 8) mentioned that, according to almost conclusive evidence of all known facts, each of the carbon-atom's four valencies is of equal value, and that no *chemical* difference results from the way we arrange the linkings around a carbon-atom. It is a matter of taste, or convenience, which carbon-atom we prefer to consider ending the chain, as far as chemical properties are concerned; the remaining part of the chain must be looked upon as a side-chain.

In the secondary propyl-alcohol we may regard as an end-link that carbon-atom to which the hydroxyl is joined, and which has then on the other three sides respectively a methyl, a methyl, and a hydrogen-atom. We can arrange the three linkings in this way:

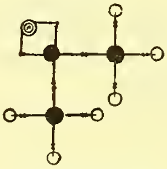
Fig. 518



Secondary propyl-alcohol

By now removing the two hydrogen-atoms as indicated, the ketone will have this form:

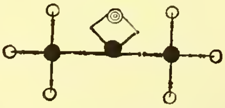
Fig. 519



Di-methyl-ketone

and stretching out the pendulous methyl-leg to a horizontal position, a perfectly legitimate operation, we have the figure as represented above.

Fig. 520

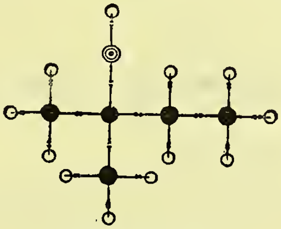


Di-methyl-ketone

I have gone so fully into the explanation of this seeming sleight of hand, because we shall constantly meet with ketones formed in the same way, and I do not like my readers to think that I am unduly trying the patience of 'the long suffering' paper.

We may now proceed to the third case, hydrogen-peroxide's reaction on tertiary alcohols. For that purpose we take the tertiary amylene-hydrate (fig. 348, p. 72).

Fig. 521



Amylene-hydrate

As the hydroxyl's carbon-atom is surrounded on all other sides by carbon-atoms, neither aldehyde nor ketone can be formed, because the former requires for its formation two, and the latter one, removable hydrogen-atoms directly connected with the hydroxylic-carbon-atom.

In order to get a free valency to satisfy the cravings of the oxygen-atom, after hydrogen-peroxide has deprived it of its hydrogen, it has no other expedient but to sever its connection with the part of the chain next to the hydroxyl.

Hydrogen-peroxide now reacts also on the part split off, takes away one of its hydrogens, and another hydrogen-peroxide splits up into three parts: a hydrogen, an oxygen-atom, and a hydroxyl. The two latter occupy the vacancies. The process rendered in words seems rather complicated, but an illustration will show how simple it really is.

Fig. 522

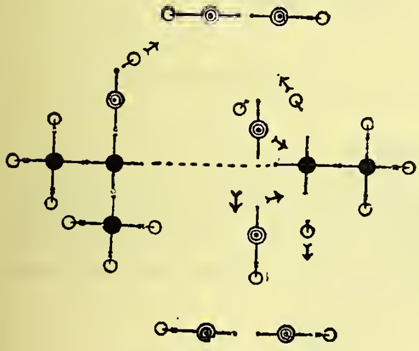
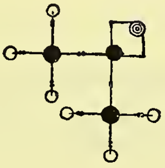


Fig. 523

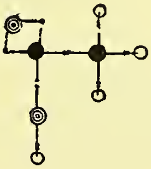


Di-methyl-ketone

Water

Water

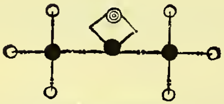
Fig. 524



Acetic acid

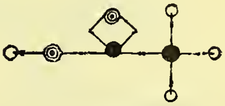
Legs outstretched:

Fig. 525

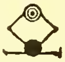
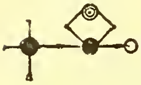
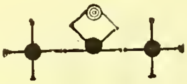


Di-methyl-ketone

Fig. 526



Acetic acid

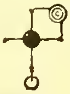
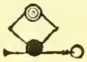
It will readily be seen that hydrogen-peroxide reacts exactly in the same way on all three sorts of alcohol; that the results turn out to be of different characters is entirely due to the presence and number of hydrogen-atoms attached to the carbon-atom attacked, or to their absence. In all cases the figure FIG. 527  (carbonyl) is formed; in aldehydes it is accompanied by one hydrogen-atom FIG. 528 , in ketones by none FIG. 529 ; we can, therefore, always recognise an aldehyde by the former figure, and a ketone by the latter.

An aldehyde can never be formed from the benzene-nucleus itself; as three of the carbon-atom's valencies in aldehyde are taken up by the oxygen and hydrogen, there is only one valency left free for joining other atoms in a chain; that chain must, therefore, by necessity, be an open one, and the aldehyde-carbon must always form the end-link in the chain.

A ketone-link, on the other hand, having two valencies free, can form a link in both open and closed chains, but can never form an end-link.

## SPECIFICATION

# ALDEHYDES

*Index*, FIG. 530  or FIG. 531  *Chemical symbol*, CHO

## 1. Aliphatic Aldehydes

### a. Aldehydes from Paraffins

Though every primary alcohol is capable of forming an aldehyde, not many have been prepared. The first of these is formed from *methyl-alcohol* (fig. 336, p. 69).

FIG. 532

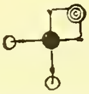
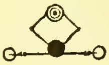


FIG. 533



Methyl-aldehyde, formic aldehyde, formaldehyde, $CH_2O$; a gas; antiseptic, more powerful than corrosive sublimate (*Compt. Rend.* cxiv. p. 1278); it is remarkable as the compound from which a carbohydrate (sugar group, *vide* p. 153) was first synthetically prepared

Methyl-aldehyde is strongly inclined to polymerise (*vide* p. 32), so much so that it has hitherto been impossible to prepare the pure aldehyde. To make this polymerisation process better understood, we shall have to resort to the perspective drawing of the aldehydes. If we look upon the formation of methyl-aldehyde as derived from methyl-alcohol by abstracting that hydrogen which is opposite the hydroxyl, we have a figure which perhaps is more correct, but less perspicuous because perspective.

Fig. 534

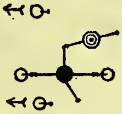
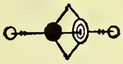
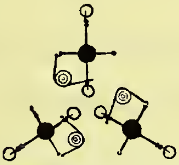


Fig. 535



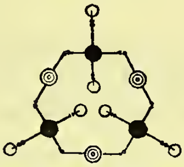
Now as to the polymerisation, three of these join and form a ring-shaped compound, paraformic aldehyde:

Fig. 536



Three molecules methyl-aldehyde

Fig. 537



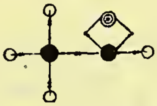
Paraformic aldehyde, tri-oxy-methylene, $C_3H_6O_3$; m.p. 152–172°

Formalin is a 40 per cent. aqueous solution of formaldehyde.

Formalith is kieselguhr impregnated with formalin.

The next aldehyde is formed from *ethyl-alcohol* (fig. 337, p. 70).

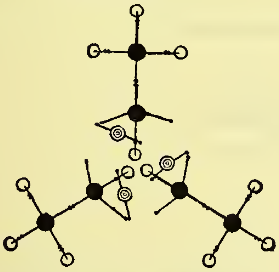
Fig. 538



Acetic aldehyde, aldehyde, $C_2H_4O$; b.p. 21°; inhaled produces cramp in the throat; antiputrescent; used in the manufacture of *aldehyde green*

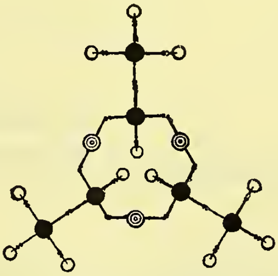
It is a by-product obtained in large quantities in the manufacture of spirit. It left to itself, it changes into a polymerised compound, paraldehyde, but not so readily as methyl-aldehyde. The process, however, is analogous, and may be illustrated thus:

Fig. 539



Three molecules aldehyde

Fig. 540



Paraldehyde, $C_6H_{12}O_3$; m.p. 10–12°; b.p. 125°; hypnotic, antidote to strychnine, diuretic, used internally and hypodermically

If the same three molecules of aldehyde were put together in a slightly different way, they would form benzene.

Fig. 541

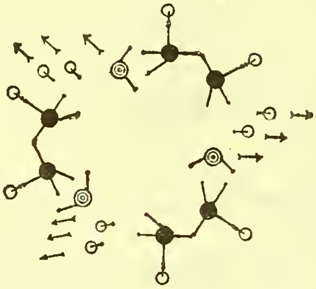
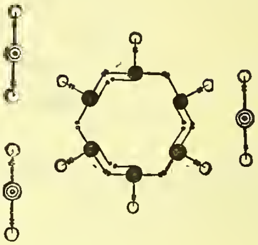


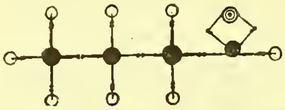
Fig. 542



This is theory; the slightly different way has yet to be discovered; but it is not impossible that nature knows something about it.

Amongst the other aldehydes from mon-acid alcohols may be mentioned **butyr-aldehyde**:

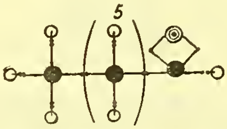
Fig. 543



Normal butyr-aldehyde, $C_4H_8O$; b.p. 73°

Fig. 544

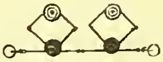
From *heptyl-alcohol* (fig. 350, p. 72):



Œnanthol, $C_7H_{14}O$; b.p. 152–155°

From *di-acid alcohols,* di-aldehydes are in the same way derivable; for instance, from ethylene-glycol (fig. 364, p. 76).

Fig. 545

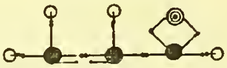


Glyoxal, oxal-aldehyde, $C_2H_2O_2$; deliquescent mass

## b. Aldehydes from Ethylenes

From *allyl-alcohol* (*vide* fig. 352, p. 73) is derived

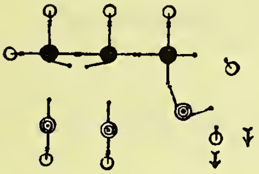
Fig. 546



Acroleïn, allyl- or acryl-aldehyde, $C_3H_4O$; b.p. 52°·4

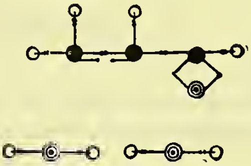
Acroleïn is also (and practically) formed from glycerin (fig. 375, p. 78) by water abstraction.

Fig. 547



Glycerin – two molecules of water

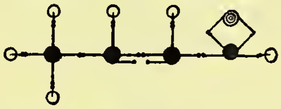
Fig. 548



Acroleïn + two molecules of water

From *crotyl-alcohol* (fig. 353, p. 73):

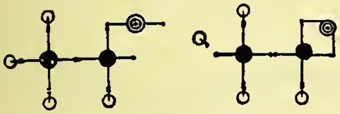
Fig. 549



Croton-aldehyde, $C_4H_6O$; b.p. 104°

Croton-aldehyde may also be formed from two molecules of aldehyde, which first polymerise, forming an intermediate compound aldol, and then lose a molecule of water

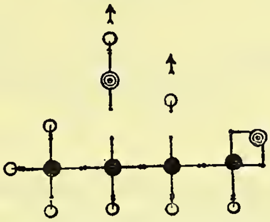
Fig. 550



Two molecules aldehyde

=

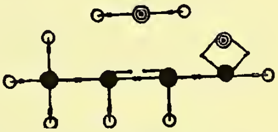
Fig. 551



Aldol, β-hydroxy-butyr-aldehyde less one mol. water, syrupy liquid; b.p. 90-105°; 20 mm.

=

Fig. 552

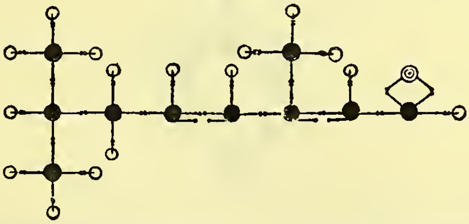


Croton-aldehyde

Singly-linked compounds containing hydroxyl besides the aldehyde-group are collectively termed *aldols* (contracted from aldehyde-alcohol). When each carbon-atom, except the aldehyde index, is provided with a hydroxyl, the compound is termed a *carbohydrate.*

From *geraniol* (*vide* fig. 356, p. 74):

Fig. 553



Geranial, $C_{10}H_{16}O$ (*Ph. C.* xxxii. p. 221; *Ber.* xxiv. p. 205); constituent of oil of orange peel, of citronella, lemon, &c.

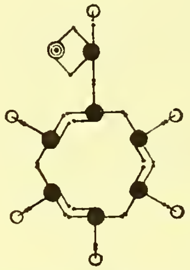
## 2. Aldehydes from Cyclo-compounds

Benzene itself cannot form an aldehyde (*vide* p. 130).
A few aldehydes derived from benzene-alcohols have a claim on our attention.

### a. Aldehydes from Benzene and Paraffin

From *benzyl alcohol* (fig. 394, p. 84) an important aldehyde is derived—oil of bitter almonds.

Fig. 554

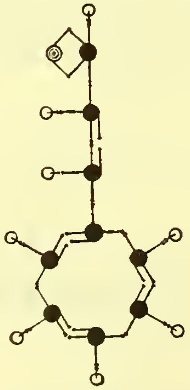


Benzoic aldehyde, benz-aldehyde, oil of bitter almonds, $C_7H_6O$ ; b.p. 179° ; is prepared on a large scale from toluene (fig. 232, p. 44)

### b. Aldehydes from Benzene and Olefine

From *styrone, cinnamic alcohol* (fig. 413, p. 90):

Fig. 555

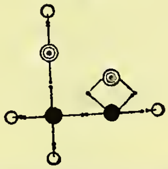


Cinnamic aldehyde, phenyl-acroleïn, $C_9H_8O$ ; b.p. 247° ; is the chief constituent of oil of cinnamon

## 3. Alcohol-aldehydes

The aldehydes just discussed were formed from mon-acid alcohols, or benzene alcohols, but poly-acid alcohols and phenol alcohols can form aldehydes as well; with their alcoholic hydroxyls they possess, however, at the same time, the character of an alcohol, or phenol, and an aldehyde. We have already seen the formation of one of the alcohol-aldehydes, aldol (fig. 550, p. 133), and we shall see more of them collected into one group, the carbohydrates (p. 151). There is now only one more to mention: glycollic aldehyde, derived from *ethylene glycol* (fig. 364, p. 76):

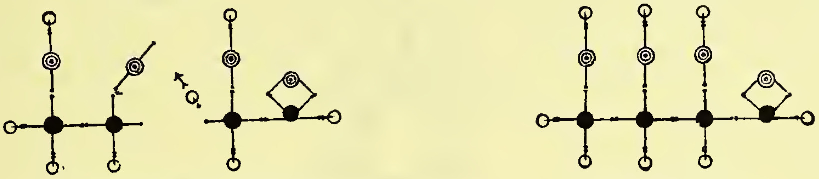
Fig. 556



Glycollic aldehyde, $C_2H_4O_2$, syrupy liquid

It has not been isolated yet, and is known only in aqueous solution. It has the property so characteristic of aldehydes, that of polymerising (*Ber.* xxv. p. 2549).

Fig. 557 Fig. 558



Two molecules glycollic aldehyde = Erythrose $C_4H_8O_4$

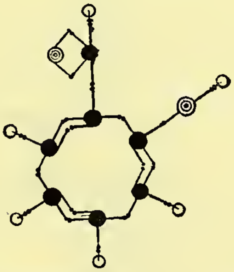
Erythrose is a tetrose, a carbohydrate.

For those alcohol-aldehydes which are known as carbohydrates *vide* p. 151.

## 4. Phenol-aldehydes

From *saligenin* (fig. 461, p. 106):

Fig. 559

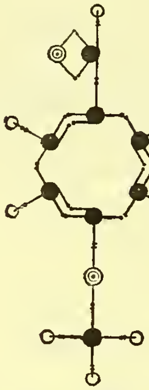


Salicylic aldehyde, $C_7H_6O_2$; b.p. 196°

is contained in the flowers of the different varieties of *Spiræa.*

From *anisic alcohol* (fig. 509, p. 122) we obtain a phenyl-aldehyde-ether:

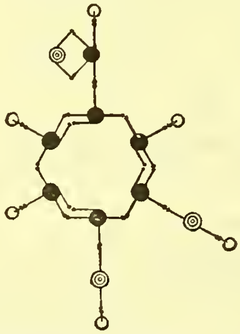
Fig. 560



Anisic aldehyde, methoxy-benz-aldehyde, $C_8H_8O_2$; b.p. 247°

and from *protocatechuic alcohol* (fig. 463, p. 106) a phenol-aldehyde:

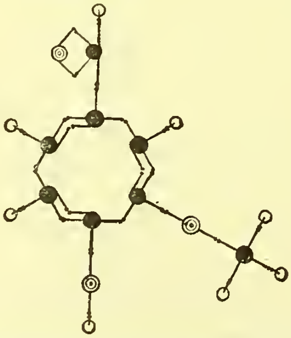
Fig. 561



Protocatechu-aldehyde, $C_7H_6O_3$; m.p. 150°

From *vanillic alcohol* (fig. 510, p. 123) by oxidation, or from *protocatechu-aldehyde* (above) and *methyl alcohol* in meta-position is formed a phenol-aldehyde-ether:

Fig. 562



Vanillin, methyl-protocatechuic aldehyde, $C_8H_8O_3$; m.p. 80°

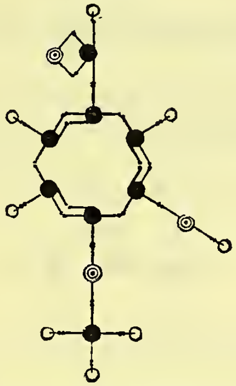
Vanilla owes its aroma to vanillin, the crystalline coating on the fruit of the vanilla. It is now made artificially on a large scale from the cambium sap of firs and pines (*vide* coniferyl alcohol, fig. 511, p. 123), or from iso-eugenol (fig. 503, p. 120). It may also be prepared from wood-tar (*vide* guaiacol, fig. 499, p. 118).

The preparation of artificial vanillin from coniferyl alcohol is based upon the curious behaviour of all benzene-compounds, with an aliphatic radical as side-chain, no matter what this radical may be, whether a long or a short chain, a saturated or unsaturated radical; on oxidation the whole chain is pulled to pieces right down to the last carbon-atom, which, however, remains with the benzene-ring. The chain is converted into acet-aldehydes, acetic or carbonic acid; the carbon-atom remaining with the benzene-ring is transformed into carboxyl or aldehyde according to the force of oxidation. In the case of coniferyl-alcohol the allyl-radical is burnt down, as it were, to formic aldehyde.

Vanillin is besides found in the beet sugar, asparagus, Siam benzoin, and asafœtida in small quantities.

If we join methyl-alcohol to the para- and not to the meta-hydroxyl in protocatechu-aldehyde we obtain

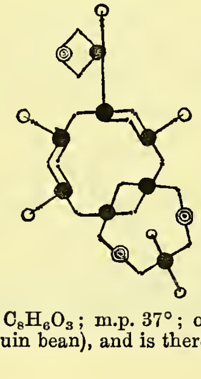
Fig. 563



Iso-vanillin, $C_8H_8O_3$; m.p. 115°; a recently patented compound (*Ph. C.* xxxii. p. 78)

When we abstract two hydrogen-atoms from methyl and hydroxyl in vanillin or iso-vanillin, exactly as we performed the operation on eugenol in order to obtain safrol (*vide* fig. 504, p. 120), the result is a compound termed piperonal.

Fig. 564

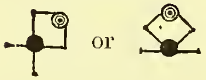


Piperonal, protocatechu-aldehyde-methylene-ether, $C_8H_6O_3$; m.p. 37°; occurs in the seeds of *Piper nigrum*; antiseptic and antipyretic; smells strongly from coumarin (Tonquin bean), and is therefore used in the perfumery trade as heliotropin

# KETONES

FIG. 565

*Index*,



or

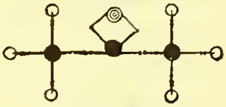
Carbonyl

Ketones may be formed from alcohols, benzene-alcohols, phenols, and phenol-alcohols (*vide* p. 130).

## 1. Ketones from Alcohols

A ketone must have at least three carbon-atoms, and the alcohol from which it is to be formed must be a secondary alcohol; consequently the first ketone we meet with is derived from *secondary propyl-alcohol* (fig. 339, p. 70).

FIG. 566

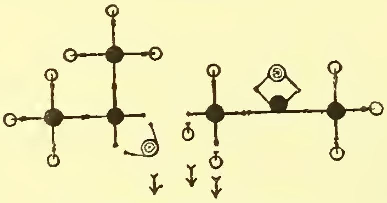


Acetone, di-methyl-ketone, $C_3H_6O$; b.p. 56°·5

Unlike aldehydes the ketones do not polymerise, but their most remarkable property is an inclination to *condense*, i.e. two or more molecules join, with *elimination of water* forming a new compound.

Thus two molecules of acetone condense forming mesityl-oxide:

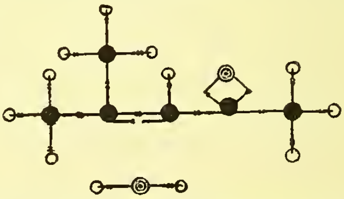
FIG. 567



Two molecules of acetone

=

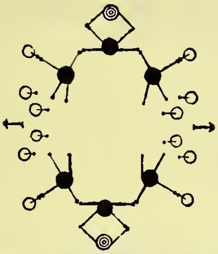
FIG. 568



Mesityl-oxide, iso-propylidene-ketone, $C_6H_{10}O$; b.p. 130°; peppermint-smell

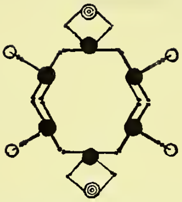
By eliminating hydrogen instead of water we (theoretically) form quinone (*vide* fig. 584, p. 142), also, perhaps, one of Nature's inscrutable ways which we have not yet succeeded in imitating.

Fig. 569



Two molecules of acetone

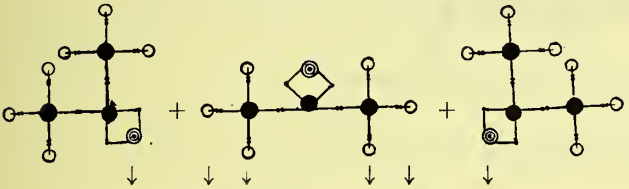
Fig. 570



Quinone, $C_6H_4O_2$ ; m.p. 116°

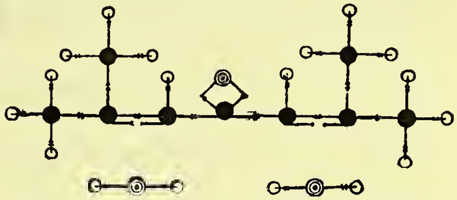
If three molecules of acetone join, and two molecules of water are eliminated, we obtain a compound termed **phorone**

Fig. 571



Three molecules of acetone

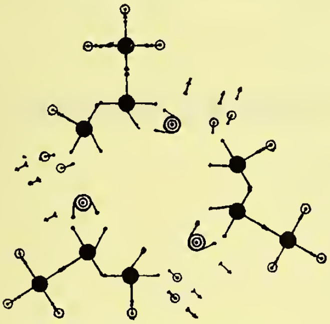
Fig. 572



Phorone, acetophorone, $C_9H_{14}O$ ; m.p. 28°[1]

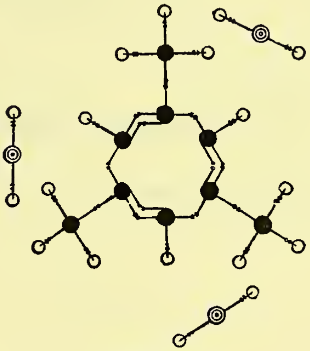
By elimination of three molecules of water we obtain **mesitylene** (*vide* fig. 242, p. 45)

Fig. 573



Three molecules of acetone

Fig. 574



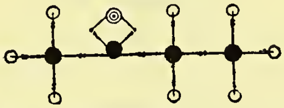
Mesitylene

Assisted by this remarkable property of the ketones, it has been possible synthetically to build up a number of cyclo-derivatives.

**Mixed ketones** are those which have a different number of carbon-atoms on each side of the carbonyl.

From *methyl-ethyl-carbinol*:

Fig. 575



Methyl-ethyl-ketone, $C_4H_8O$ ; b.p. 81°

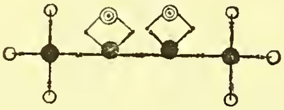
---

[1] Some text-books give to phorone the structure $(CH_3)_2C=CH-C(CH_3)=C.H-CO-CH_3$, but having regard to its formation from a compound, nitrosotriacetonamine, the above structure appears more probable (vide *R. & S.* I. p. 573, and *Beilst*, i. p. 822 ; also *Ber.* xiv. p. 352).

Di-ketones are formed from *di-acid alcohols.*

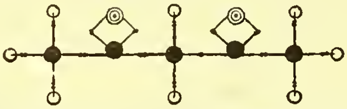
They are distinguished as α-, β-, or γ- (1 : 2, 1 : 3, 1 : 4) di-ketones, according as the carbonyl-groups are close together or separated by one or two carbon-atoms.

Fig. 576



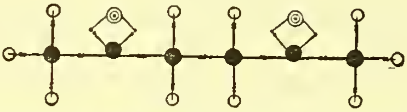
Di-acetyl, di-keto-butane, $C_4H_6O_2$ ; b.p. 87° ; α-di-ketone

Fig. 577



Acetyl-acetone, $C_5H_8O_2$ ; b.p. 136° ; β-di-ketone

Fig. 578

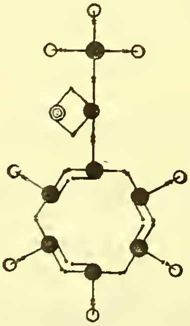


Acetonyl-acetone, $C_6H_{10}O_2$ ; b.p. 187° ; γ-di-ketone

## 2. Ketones from Benzene-alcohols (Phenones)

From *methyl-phenyl-carbinol* (fig. 397, p. 85) is derived

Fig. 579

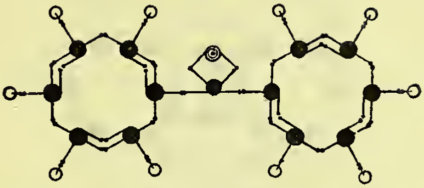


Aceto-phenone, hypnon, methyl-phenyl-ketone, acetyl-benzene, ethyl-phenyl-acetone, $C_8H_8O$ ; m.p. 20°·5 ; hypnotic

It may also be considered as acetone in which one of the methyls is exchanged for phenyl, or as a combination of acetic acid and benzene by separation of water; hence the various names.

From *di-phenyl-carbinol* (fig. 408, p. 88):

Fig. 580



Benzophenone, diphenyl-ketone, $C_{13}H_{10}O$; m.p. 48°; the mother substance of *auramine*, a yellow dye; may be considered acetone in which both methyl-groups are replaced by phenyls

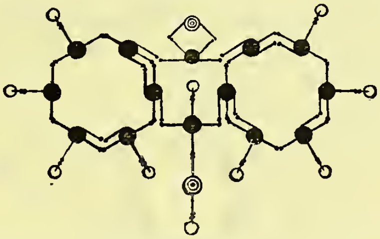
If a methyl-group is joined in para-position to one of the phenyls above (converting it into toluene, fig. 232, p. 44), the compound—benzo-para-cresol—is found to be a powerful antiseptic (*Nouv. Remèdes*, 1893, No. 4): it has its name from para-cresol entering into its preparation.

## 3. Ketones from Anthracene-alcohols

Theoretically and actually, there are two, and they are formed from *β-hydroxy-anthranol* (*vide* fig. 415, p. 91).

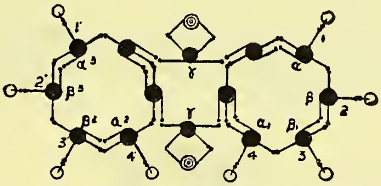
In oxanthranol the ketone is formed from *one* of the alcohol groups (hydroxyls); in anthraquinone from *both*.

Fig. 581



Oxanthranol, anthra-hydroquinone, $C_{14}H_{10}O$; m.p. not ascertained

Fig. 582

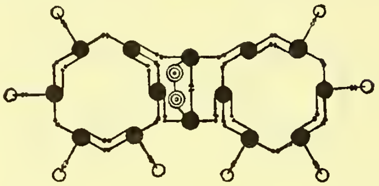


Anthraquinone, $C_{14}H_8O_2$; m.p. 273–285°; yellow crystals

Though perhaps the great majority of chemists accept this structure as the true one, it is not admitted as such by all of them. They all acknowledge that the oxygen-atoms are joined to those carbon-atoms represented above, but some are of the opinion that the oxygen-atoms are, moreover, linked together.

That can be drawn only perspectively:

Fig. 583



Anthraquinone

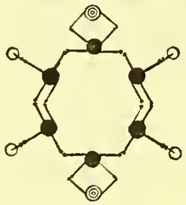
According to this formula anthraquinone would be a peroxide of something.

To judge from most of its properties (it behaves generally like a di-ketone), and from its several derivations, the di-ketone formula seems to be the more probable. There is, however, always the possibility of the compound changing structure according to circumstances (tautomerism, *vide* p. 93), thus reconciling both views. This diversity of opinion causes some embarrassment to the illustrator; if anthraquinone is a di-ketone, it should evidently be represented as three interlocked benzene-rings (comp. fig. 416, p. 91); if not, fig. 583 would be the correct interpretation. I have chosen a middle course, represented in fig. 582, because it reminds one of its derivation from anthracene, and of the two views of its structure, though I am not sure that this is sufficient justification for such a halting representation.

## 4. Ketones from Phenols

From *hydroquinone* (fig. 420, p. 92) is formed a di-ketone, quinone (*vide* fig. 570, p. 139).

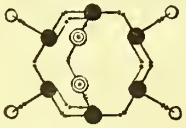
Fig. 584



Quinone, $C_6H_4O_2$; m.p. 116°; yellow crystals

It will be seen that this formation necessitates a re-arrangement of benzene's double bonds. Some chemists advocate a structure analogous to that of *anthraquinone* (fig. 583, above), so that the benzene-bindings are left undisturbed:

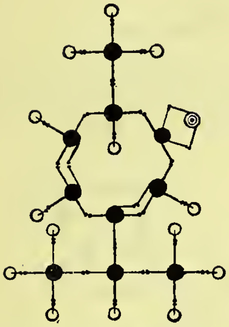
Fig. 585



Quinone

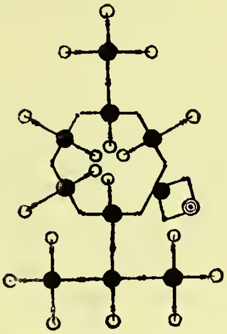
From *carvacrol* (fig. 433, p. 97), *menthol* (fig. 438, p. 98), and *Borneo camphor* (fig. 439 &c., p. 98) are formed:

Fig. 586



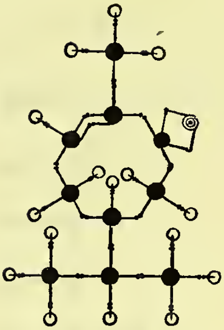
Carvol, $C_{10}H_{14}O$; b.p. 227°; chief constituent of oil of cumin

Fig. 587



Menthone, $C_{10}H_{18}O$; b.p. 206°

Fig. 588

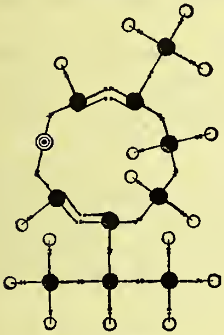


Common or Japan camphor, $C_{10}H_{16}O$; m.p. 175°

Some authorities place the ketone group in *m*-position in carvol, and in *o*-position in menthone. In that case the hydrogen inside the ring in carvol must be placed in *p*-position, and the double bonds re-arranged accordingly.

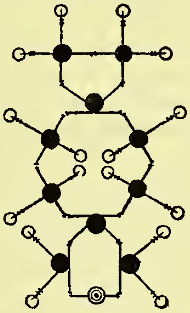
Much discussion has been, and is still, going on regarding the structure of camphor. The above is Kekulé's, and subjoined I give some of the others.

Fig. 589



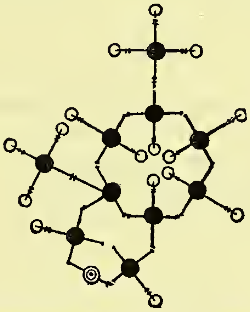
Victor Meyer, *Ber.* iii. p. 116

Fig. 590



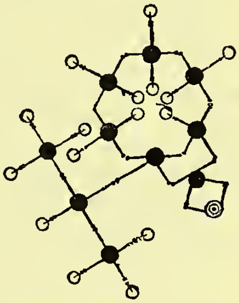
Hlasiwetz, *Ber.* iii. p. 540

Fig. 591



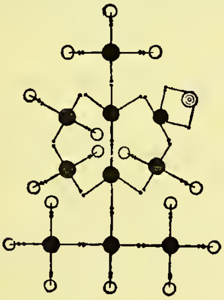
Armstrong, *Ber.* xi. p. 1698

Fig. 592



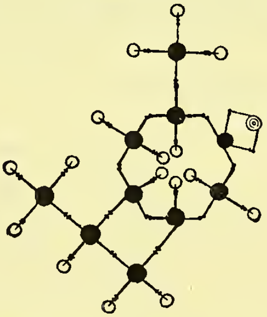
Kachler, *Ann.* clxv. p. 185

Fig. 593



Wallach, *Ann.* ccxxx. p. 269; Kanonnikow, *Ber.* xvi. p. 3051; Bruhl, *Ber.* xxi. p. 469

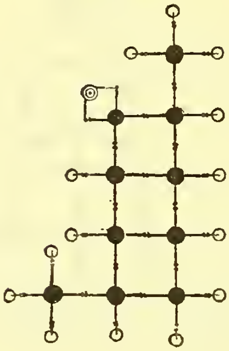
Fig. 594



Norman Collie, *Ber.* xxv. p. 1114

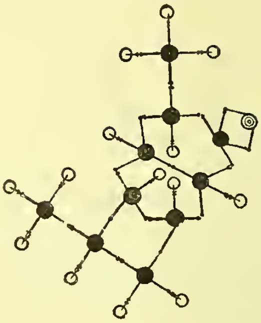
Norman Collie (*loc. cit.*) gives the following structure of carvol:

Fig. 595



which brought into hexagonal configuration with diagonal bond for the sake of the better comparison with the others would look like this (*vide* diagonal bond, p. 53):

Fig. 596



Carvol (Norman Collie)

One of the difficulties of finding a satisfactory structural formula for camphor and some allied compounds is this. The specific refractive power[1] of a compound is made up of the sum of the refractive powers of its constituents, provided the four valencies of every carbon-atom in the compound are singly bound. But if two or three valencies of any carbon-atom are linked to one and the same atom, as in the case of aldehydes, ketones (to oxygen), benzenes, olefines, and acetylenes (to another carbon-atom), every double bond is found to increase the refractive power and every triple bond still a little more.

Now, whilst benzene and its derivatives have a molecular refraction corresponding to three double bonds, camphor has a refractive power, suggesting no double linkage between the carbon-atoms in the compound, i.e. all the carbon-atoms in camphor are united by single bonds. That is one of the reasons why so many eminent chemists have tried their strength on the structure of camphor. Kekulé's formula answers tolerably well to its chemical reactions; but there are the double bonds; the problem has therefore been to find a singly linked ring combining all the chemical advantages of Kekulé's ring. Which one is to be declared the successful winner amongst the suggestions illustrated above has still to be decided; some of them may already have been deserted by their own sires, and some, as constructed by the rule of thumb of our symbols, look, it must be admitted, rather remarkable.

Thiocamf. Camphor can be made to absorb sixty times its volume of sulphurous acid, giving it off again on exposure. Camphor is by the absorption converted into a fluid termed *thiocamf*, and used for fumigation as a disinfectant.

Alantol, $C_{10}H_{16}O$ ($C_{20}H_{32}O$, *Ph. C.* xxviii. p. 123), b.p. 200°, is, according to the first empirical formula, supposed to be an isomer of camphor: it is found in the root of *Inula helenium*, and is used in phthisis as a substitute for creasote and oil of turpentine. Constitution not known.

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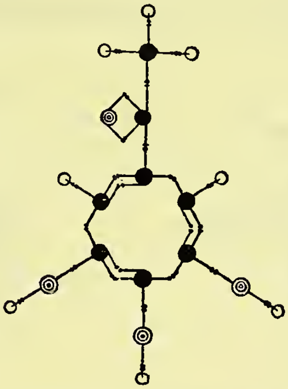
[1] If $n$ is the refractive index of a liquid, and $d$ its density, then the quotient $\frac{n^2-1}{(n^2+2)d}$ is its specific refractive power.

## Ketones from Phenol-alcohols

If we introduce into acetophenone the three hydroxyls of pyrogallol (fig. 421, p. 93) we obtain a phenone (*vide* p. 140), derived from an alcohol not yet known:

Fig. 597



Gallacetophenone, tri-hydroxy-acetophenone, $C_8H_8O_4$; m.p. 168°; substitute for pyrogallol; antiseptic, non-poisonous

## Ketones from Anthracene-phenol-alcohols

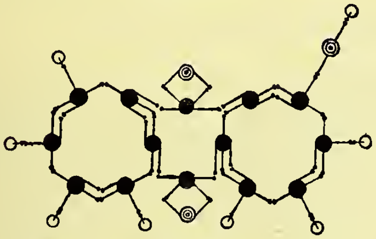
These ketones are derivable from corresponding anthracene-phenol-alcohols, with two alcoholic hydroxyls (*vide* p. 107), of which, however, but one (quinizarin-hydrate, *vide* p. 107) is known. We will therefore derive them from anthraquinone (fig. 582, p. 141), by introducing one, two, or three hydroxyls into the benzene-rings in various fashions.

This class of ketones are very important in the manufacture of dyes.

### Ketones with one Hydroxyl

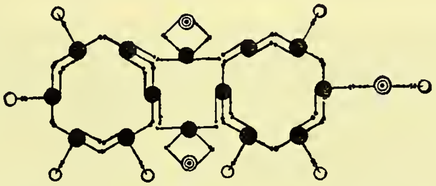
One hydroxyl may replace either an $\alpha$- or a $\beta$-hydrogen

Fig. 598



Erythro-oxy-anthraquinone, $C_{14}H_8O_3$; m.p. 190°; orange-red crystals

Fig. 599



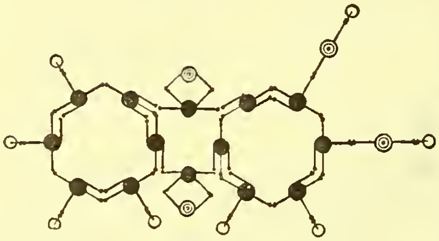
Hydroxy-anthraquinone, $C_{14}H_8O_3$; m.p. 323°; yellow crystals

## Ketones with two Hydroxyls

Ten isomers are possible, and they are all known. Four have the hydroxyls in the same benzene, and six have them in different rings.

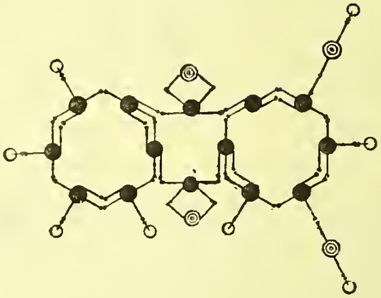
### HYDROXYLS IN THE SAME BENZENE-RING

Fig. 600



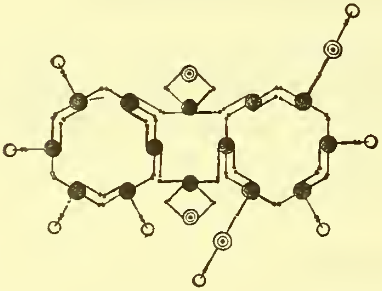
Alizarin, $C_{14}H_8O_4$; m.p. 289–290°; magnificent red crystals; the most important constituent of the madder-root; gives with metallic oxides or in combination with other compounds a number of different dyes

Fig. 601



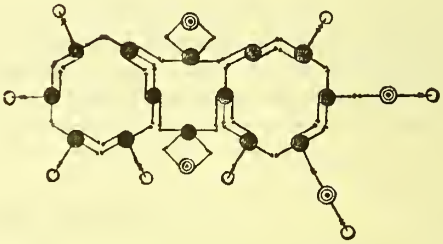
Xantho-purpurin, purpur-oxanthin, $C_{14}H_8O_4$; m.p. 263°; yellow crystals; is also present in the madder-root

Fig. 602



Quinizarin, $C_{14}H_8O_4$; m.p. 195°; beautiful bright-red crystals; forms with metallic oxides 'lac-dyes'

Fig. 603



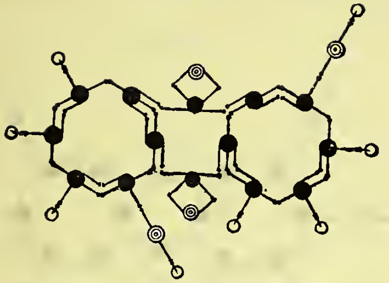
Hystazarin (Iso-alizarin ?), $C_{14}H_8O_4$

The six possible isomers[1] with the two hydroxyls in different benzene-nuclei are:

---

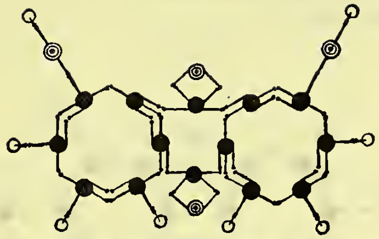
[1] Anthrarufin, anthraflavic acid, and benz-dioxy-anthraquinone are all of them formed from *m*-hydroxy-benzoic acid, and must therefore share among them the only three possible structures as represented by figs. 604, 606, and 608. Anthrarufin can only have the structure represented by fig. 604, because it splits up, as before mentioned, into salicylic and *m*-hydroxy-benzoic acids; the two other structures cannot yield salicylic acid, and are more difficult to decide between. I have given fig. 606 to anthraflavic acid, because its formation from *m*-hydroxy-benzoic acid appears more natural and simple than that of the other structure; and this agrees with the fact that anthraflavic acid is the chief product from *m*-hydroxy-benzoic acid. Chrysazin, like anthrarufin, splits up into salicylic acid and *m*-hydroxy-benzoic acid, from which latter, however, it cannot be derived; consequently it has either the structure of fig. 607 or that of fig. 605, and no facts are known to favour one structure more than the other. As, however, fig. 607 is more nearly related to the structure given to anthraflavic acid than fig. 605, I have assigned it to iso-anthraflavic acid. The last structure (fig. 609) has then no choice, but frangulinic acid.

Fig. 604



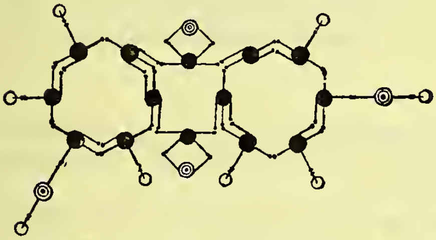
Anthrarufin, $C_{14}H_8O_4$; m.p. 280°

Fig. 605



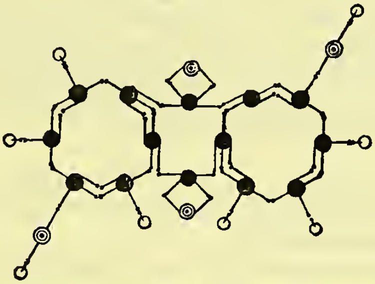
Chrysazin, $C_{14}H_8O_4$; m.p. 191°

Fig. 606



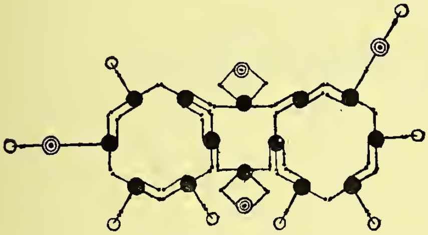
Anthraflavic acid, $C_{14}H_8O_4$; m.p. above 330°

Fig. 607



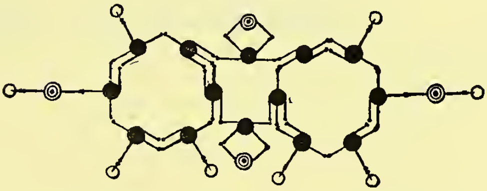
Iso-anthraflavic acid, $C_{14}H_8O_4$; m.p. above 330°.

Fig. 608



Benz-dioxy-anthraquinone, $C_{14}H_8O_4$; m.p. 291°

Fig. 609

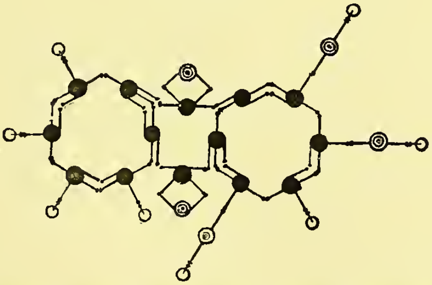


Frangulinic acid, $C_{14}H_8O_4$; m.p. 252°; occurs as a glucoside in the bark of *Rhamnus frangula*

## Ketones with three Hydroxyls

Though there are fourteen possible isomers, five of which are known, we shall limit ourselves to illustrating the most important of them:

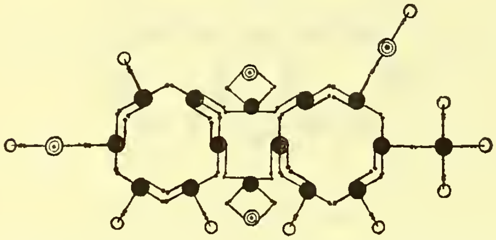
Fig. 610



Purpurin, $C_{14}H_8O_5$; m.p. 253°; yellow crystals; with metallic oxides produces dyes; is found in the madder-root

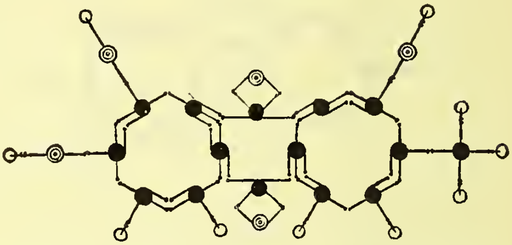
From *m*-methyl-anthraquinone there are two ketones of interest; one with two, the other with three hydroxyls:

Fig. 611



Chrysophanic acid, $C_{15}H_{10}O_4$; m.p. 162°; gold-coloured crystals; occurs in the rhubarb-root, senna, and many lichens; is obtained from chrysarobin (*vide* p. 122) by oxidation; was formerly much used in skin diseases; by *acidum chrysophanicum medicinale* is always meant chrysarobin; the chrysophanic acid of commerce is mixed with chrysarobin

Fig. 612



Emodin, $C_{15}H_{10}O_5$; m.p. 250°; orange-red crystals; occurs in the bark of *Rhamnus frangula*; also, together with chrysophanic acid, in the rhubarb-root (comp. frangulinic acid, fig. 609, p. 147, to which, and to chrysophanic acid, it is related)

The *m*-position of methyl is ascertained, likewise that the hydroxyls belong to different nuclei. The positions of the hydroxyls on each nucleus have not been ascertained; the representations above are arbitrary.

There are also tetra- and hexa-hydroxy-anthraquinones, and ketones from di- and tri-methyl-anthraquinones, but of less interest, as are also some ketones formed from phenantrene.

# PART V.

# Oxygen Compounds

## CARBOHYDRATES AND GLUCOSIDES

# ALCOHOL-ALDEHYDES AND ALCOHOL-KETONES

## Carbohydrates

From almost the first days of chemistry's existence the compounds we are now going to discuss were treated as of one family, because they had many similarities, both chemical and physical. It was soon found out that they all consisted of carbon, and the elements hydrogen and oxygen in the proportion in which they form water; a circumstance considered of importance before their real structure was accounted for, hence the name of carbohydrates.

It has now been ascertained that all these compounds are aldehydes or ketones, or a combination of both. They ought therefore to be treated under these several headings, but agreeably to established practice we shall leave old family traditions undisturbed.

They are classed mainly into four groups:

1. *Alcohol-aldehydes* and *alcohol-ketones*, the grape-sugar group.

By the joining of two of these under elimination of water are derived—

2. *Anhydrides* or *ethers*, the cane-sugar group.

By the joining of three of them—

3. *Constitution unknown*, the raffinose group.

By the joining of more than three of them—

4. *Constitution unknown*, the cellulose group.

The most prominent members of these groups are:

| Grape-sugar group<br>Aldoses and Ketoses<br>(*Aldehydes*) (*Ketones*)<br>Monosaccharides, Glucoses, or Monoses | | Cane-sugar group<br>Di-hexoses<br>(*Anhydrides*)<br>Disaccharides, Saccharoses, or Bioses, $C_{12}H_{22}O_{11}$ | Raffinose group<br>Tri-hexoses<br>(*Constitution not ascertained*)<br>Trisaccharides, Raffinoses, $C_{18}H_{32}O_{16}$ | Cellulose group<br>Poly-hexoses<br>(*Constitution not ascertained*)<br>Celluloses, Polysaccharides, and Amyloses, $(C_6H_{10}O_5)_n$ |
|---|---|---|---|---|
| Trioses, $C_3H_6O_3$ . . . . | Glycerose | Saccharose | Raffinose | Cellulose |
| Tetroses, $C_4H_8O_4$ . . . . | Erythrose | Lactose | Stachyose | Starch |
| Pentoses, $C_5H_{10}O_5$ . . | Arabinose | Maltose | Melezitose | Dextrin |
| | Xylose | Trehalose | | Arabin |
| Hexoses, $C_6H_{12}O_6$ . . . . | Dextrose | Melibiose | | Sinistrin |
| | Levulose | | | Inulin |
| | Galactose | | | Glycogen |
| | Mannose | | | |
| | Sorbinose | | | |
| | Gulose | | | |
| | Acrose | | | |
| Heptose, $C_7H_{14}O_7$ | | | | |
| Octose, $C_8H_{16}O_8$ | | | | |
| Nonose, $C_9H_{18}O_9$ | | | | |

## Grape-sugar Group

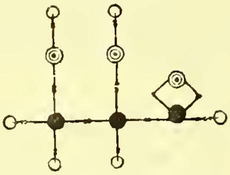
By way of variety they are also called glucoses, glycoses, or monoses, monosaccharides, and may be subdivided into *aldoses* or *alcohol-aldehydes,* and *ketoses* or *alcohol-ketones.* All have a sweetish taste.

The first of this group would perhaps be our former acquaintance, formaldehyde (fig. 532, p. 130), but as it has not any hydroxyl joined to it, there may be a doubt whether it can be naturalised, though it otherwise has the qualification of being a carbohydrate, $CH_2O$. We shall, however, see that when several of them join, they are recognised as native-born citizens of this dominion (*formose*).

The next one would be glycollic aldehyde (fig. 556, p. 135), but it exists only in aqueous solution. Polymerised, however, it forms erythrose, a tetrose (*vide* p. 135).

The next alcohol-aldehyde likely to be a carbohydrate is one derived from glycerin (fig. 375, p. 78), which, gently oxidised, forms an alcohol-aldehyde :

Fig. 613

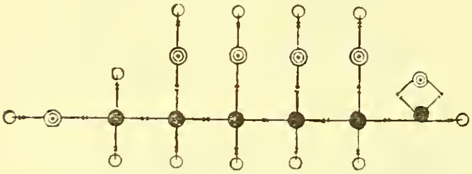


Glycerose, $C_3H_6O_3$

but neither is this known except in solution. Polymerised it forms *glucoses* (*vide* p. 154).

Tetroses (erythrose, *vide* above, and fig. 558, p. 135) and pentoses are of lesser importance, and passing them we arrive at hexoses, of which there are many species, each with several varieties. They are all derived from hex-acid alcohols (fig. 380, p. 80), by oxidising them to aldehydes or ketones ; their general structure would therefore be either

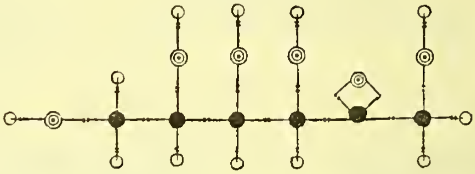
Fig. 614



Hexose (alcohol aldehyde), $C_6H_{12}O_6$ ; dextrose, mannose, gulose, derived from mannite (fig. 380, p. 80)

or

Fig. 615

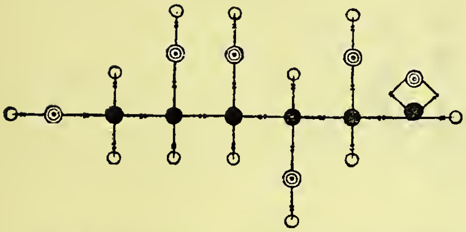


Hexose (alcohol-ketone), $C_6H_{12}O_6$ ; levulose derived from mannite ; sorbin derived from sorbitol (*vide* p. 80)

Three varieties of dextrose, mannose, and levulose are moreover known—a dextro-, a lævo-, and an inactive compound.

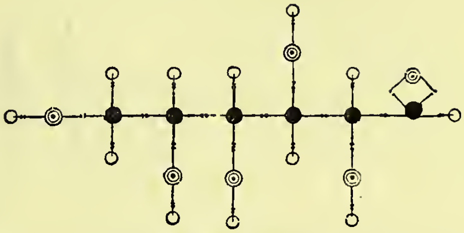
Of course there must be a difference in the structure, and guided by their behaviour in various chemical reactions the conclusion has been arrived at (*Ber.* xxiv. p. 2685) that it is not immaterial on which side of the carbon-atom the hydroxyl is placed. Thus dextrose can appear in the three varieties mentioned above, and individually their structural forms would be these.

Fig. 616



Dextrose, grape-sugar, glucose, dextro-rotatory

Fig. 617

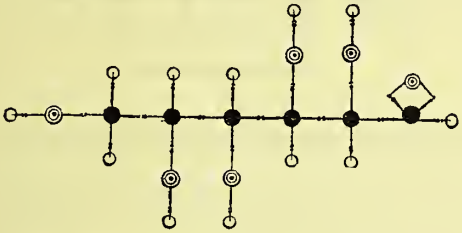


Dextrose, lævo-rotatory

It will be noticed that the hydroxyls pointing upwards in one figure turn down in the other, and *vice versa*; if an equal number of each molecule come together, they will counterbalance one another; those rays of light which by one are turned to the right are by the other turned to the left; in other words the compound will be *inactive*.

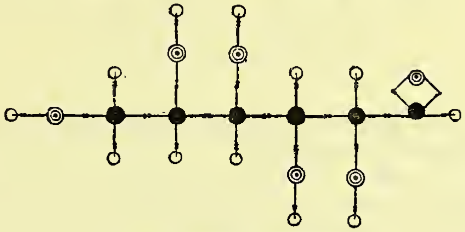
In the same manner the structure of mannose has been ascertained to be

Fig. 618



Dextro-rotatory mannose

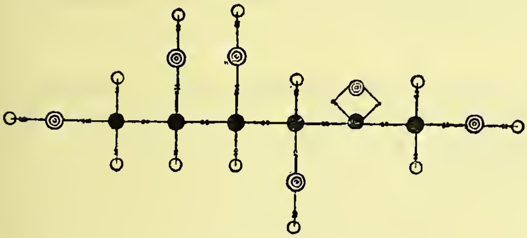
Fig. 619



Lævo-rotatory mannose

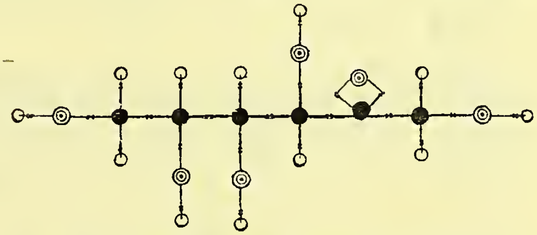
Likewise levulose, which is an alcohol-ketone

Fig. 620



Dextro-rotatory levulose

Fig. 621

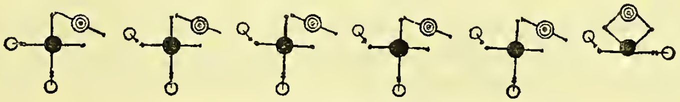


Lævo-rotatory levulose, diabetin, fruit-sugar

Dextrose and levulose are found in sweet fruits, in honey, in diabetic urine, and may be prepared from other carbohydrates; dextrose is a constituent of many glucosides.

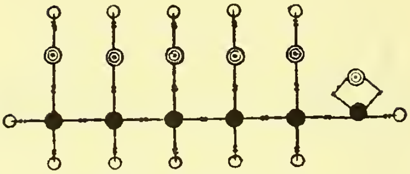
Dextrose has been synthesised from formaldehyde by polymerisation (to avoid confusion, no regard is here had to the different positions of hydroxyls).

Fig. 622



Six molecules of formaldehyde (figs. 532, 533, p. 130)

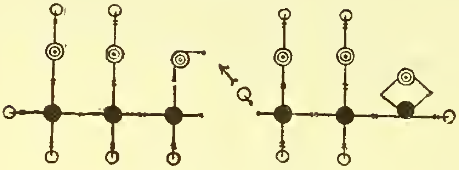
Fig. 623



Formose (dextrose ?)

Mannose from *glycerose* (fig. 613, p. 152)

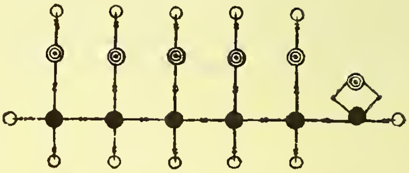
Fig. 624



Two molecules of glycerose

=

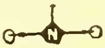
Fig. 625



α-Acrose (mannose ?)

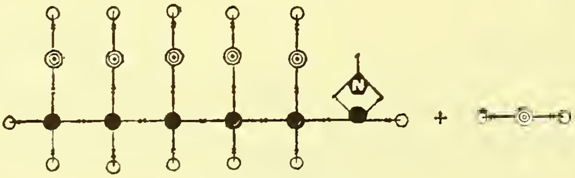
Another carbohydrate is formed at the same time, β-acrose, but its constitution has not been sufficiently investigated.

According to other authorities, glycerose, from which α-acrose has been formed, is a mixture of aldehyde-alcohol (glycerin-aldehyde) and ketone-alcohol (di-oxy-acetone); in this case α-acrose would be a mixture of levulose and mannose. The true nature of formose and acrose has, after all, not yet been fully ascertained; they seem to be mixed with several glucoses.

Dextrose may be converted into levulose in a rather circuitous way. There is a compound termed *phenyl-hydrazine* which we shall have to mention later (p. 332); its structure is rather complex, and for the sake of simplicity we shall here represent it by only one of its constituents, viz.  ($NH_2$).

When solutions of dextrose or any other sugar are heated with this compound a molecule of phenyl-hydrazine takes the place of the aldehyde-oxygen, eliminating a molecule of water, and compounds are formed which are termed *hydrazones* (p. 338)

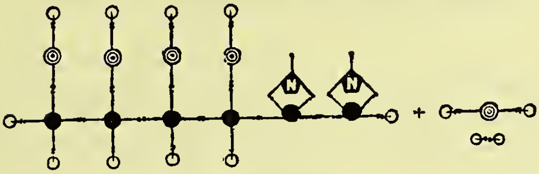
Fig. 626



Glucose hydrazone

When the action is carried further, the oxygen next in order is attacked, and must depart in form of water, taking with it two hydrogen-atoms, and another molecule phenyl-hydrazine takes its place, leaving its own two hydrogen-atoms to form a molecule: the new sort of compounds are termed *osazones* (p. 338).

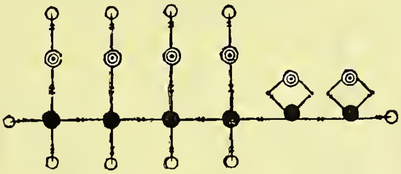
Fig. 627



Glucosazone

When acids act upon osazones, the phenyl-hydrazines are both replaced by oxygen, and compounds are formed called *osones*.

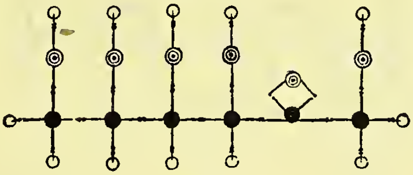
Fig. 628



Glucosone

Glucosone is poorer than levulose and dextrose by two hydrogen-atoms, and when these are added they take their place upon the end-atom, and the result is levulose.

Fig. 629



Levulose

Levulose may be reconverted to dextrose by another, also circuitous, way.

Galactose, sometimes known by the name of lactose, is derived from sugar of milk, which also is sometimes termed lactose; the two should not be confounded. Mannose is derived from *mannitol* or *mannite* (fig. 380, p. 80).

Sorbinose, or sorbin, is derivable from *sorbitol* or *sorbite* (structure not known with certainty *vide* p. 80). Gulose is a synthetically prepared compound (*vide Ber.* xxiii. p. 2628, xxiv. p. 528).

Heptose, octose, and nonose are synthetic compounds.

The glucoses are all, except sorbinose, fermentable, i.e. they are through the operations of a small micro-organism (*mycoderma cerevisiœ*) split up into alcohol and carbonic acid. That is generally represented by the equation $C_6H_{12}O_6 = (C_2H_6O)_2 + (CO_2)_2$. The mycodermæ, however, live, grow, and multiply upon the sugar; the process therefore is not quite so simple. The mycodermæ consume some of the sugar and give off again a ferment that converts the rest of the sugar chiefly into alcohol and carbonic acid, but glycerin, succinic acid, propenyl-, butyl-, and amyl-alcohols in great variety, and sometimes their ethers, are amongst the products of the mycoderma's ferment. At last, when a certain amount of these is formed, the mycodermæ are suffocated in the produce of their own excrement.

## Cane-sugar Group. $C_{12}H_{22}O_{11}$

Saccharoses, bioses, hexobioses, di-hexoses, disaccharides, are the several titles bestowed upon candy-sugar and its associates by chemists, one improving upon the other. The constitution is not fully ascertained—all that we positively know is that they are products of an aldose joining a ketose in such a way that a molecule of water is eliminated, the character both of an aldehyde and of a ketone being lost, retaining only eight of their ten hydroxyls, four of which stick to each of the two components.

The best known member in this group is, of course, cane-sugar, in which a molecule of dextrose is joined to a molecule of levulose in the way stated.

There are apparently not many ways in which this can be effected as long as we accept an open chain structure for the sugars. I give illustrations of two of them :

Fig. 630

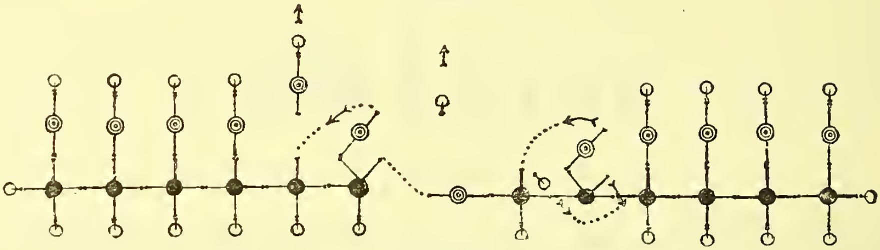
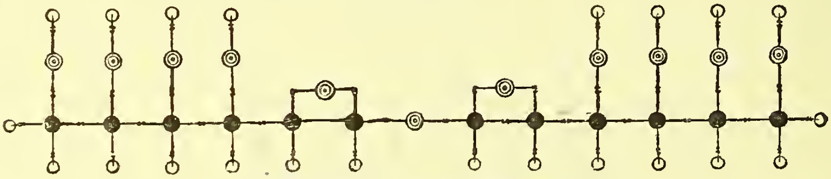


Fig. 631[1]



Cane-sugar, $C_{12}H_{22}O_{11}$, structure 1

Fig. 632

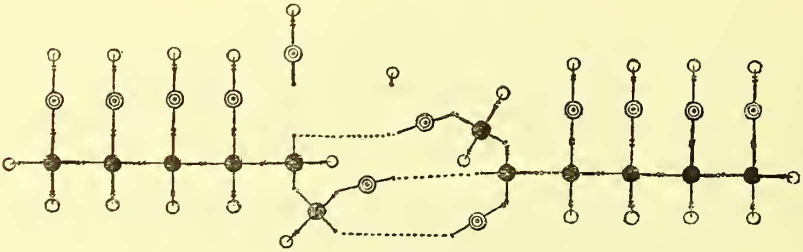
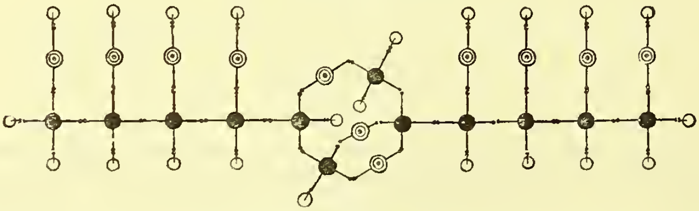


Fig. 633



Cane-sugar, structure 2

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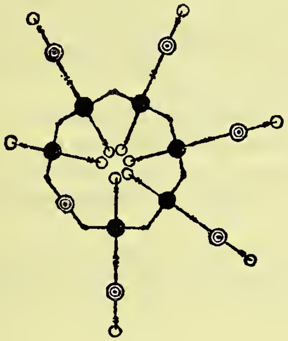
[1] For another construction of the glycide-group *vide* fig. 487, p. 115.

The first looks like etherification, the second more like anhydration. The latter is perhaps the more probable of the two, since the two hydroxyls from which water is eliminated come in direct contact in the second structure. Possibly molecular change takes place inside the hexagon, combining the two side-chains direct through the oxygen.

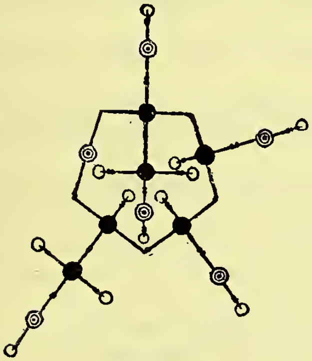
The carbohydrates have also been represented as cyclo-structures in which an oxygen-atom forms one of the links (see Tollens, *Handb. d. Kohlenhydrate*, 1888). Dextrose is thus represented as a heptagon, levulose as a pentagon, and cane-sugar as a combination of the two through an oxygen-atom left by the formation of water from two hydroxyls.

FIG. 633 A



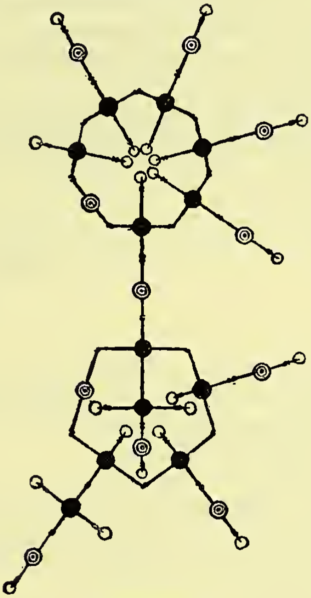
Dextrose

FIG. 633 B



Levulose

FIG. 633 C



Cane-sugar

Cane-sugar is dextro-rotatory; when heated to 210° it loses water, and is converted into caramel. Boiled with dilute acids it is split into equal parts of dextrose and levulose with assimilation of water, and is then called invert-sugar, which is lævo-rotatory. The same is effected by such ferments as diastase. Cane-sugar is not fermentable before it is broken up in this way.

Milk-sugar, *lactose*, *lactobiose*, occurs in milk, and is a combination of galactose and dextrose with the aldehyde-group left intact.

Malt-sugar, *maltose*, *malto-biose*, is found in beer.

Agavose occurs in the sap of *Agave americana* (*Amer. Ch. J.* xiv. p. 548).

A structure has been suggested (*Ber.* xxi. p. 2633) for milk-sugar combining, through abstraction of a molecule of water, the aldehyde-end of galactose with the alcoholic end of dextrose in the form of a penta-methylene in which two methylenes are replaced by oxygen-atoms. Similar structures may also be formed for the other sugars of this group, but they are mostly geometrical experiments only, without much support or refutation in known facts.

## Raffinose-group, Tri-hexoses

$C_{18}H_{32}O_{16}$

Trisaccharides and trioses are other names for this group, but the latter ought to be discontinued, as we have another triose-group amongst *glucoses* (p. 151) where this designation is more appropriate.

There are only three members of this group, but as a set-off one of them is luxuriously fitted out with names; raffinose, melitriose, melitose, gossypose, plussugar; is composed in a manner similar to that of cane-sugar, but of three glucoses, dextrose, levulose, and gallactose; its structure more particularly is not known. It occurs in manna, in cotton-seed, and in molasses from beet-sugar.

Stachyose, a recently, as tri-hexose, discovered sugar (*Ber.* xxiii. p. 1692, xxxiv. p. 2705) occurring in the root of *Stachys tuberifera*, is perhaps, according to later researches, a poly-hexose ($C_{36}H_{64}O_{32}$).

## Cellulose-group

$(C_6H_{10}O_5)_n$

The members of this group are, in the cane-sugar manner, composed of several molecules of hexoses, but how many is as yet not discovered.

Cellulose forms the membranes of vegetable cells, and is thus widely distributed in nature as the chief material of all plants.

Paper is cellulose contained in silk, linen, and cotton rags, or in esparto-grass, straw, &c.

Concentrated sulphuric acid dissolves cellulose, converting it into a compound termed *amyloid*, which is thrown down by diluting the solution.

Parchment paper is unglazed paper superficially converted into amyloid by dipping it into conc. sulphuric acid.

An inferior sort of parchment paper is made by treating the pulp already in the hollander with sulphuric acid, chloride of zinc, &c. It is by far not so tough as the genuine article, but in appearance there may be no difference.

Wood-pulp is obtained by mechanically rubbing up wood into a fine pulp.

Sulphit-cellulose is cellulose obtained as a pulp by disintegration on heating wood with calcium sulphite.

Chinese rice-paper is not prepared from rice but from the pith of *Aralia papyrifera*, a small shrub found only in Formosa.

Japanese paper is made from the long bark fibres of the paper-mulberry tree.

Tunicin is animal cellulose occurring in the tunicates.

Starch is found everywhere in the vegetable world.

The several varieties of starch (potato, maize, rice, sago, arrowroot, tapioca) are only physically distinguishable one from another; chemically they are all identical.

The investigations on starch are, up to the present, far from being conclusive. It is said to consist chiefly of two isomeric compounds, granulose and farinose. When boiled with water granulose dissolves, and farinose remains unaltered.

It is asserted by some that soluble starch has the formula $(C_{12}H_{20}O_{10})_{30}$; others make it a round 100 instead of 30. Starch is converted into dextrin, maltose, and dextrose by dilute acids. Glycogen is animal starch, found principally in the liver.

Cellulose and starch are compounds so closely allied that there is every reason to hope that the problem of transforming cellulose into starch may one day be solved. That would be an immense boon not only to the discoverer, but to the world at large. Our little globe will then be able to feed its people for more than those 182 years which an able and celebrated statistician has calculated her limits to be under present circumstances (meeting of the British Association, September 1890). And just imagine the beautifully pastoral idyl of young ladies and gentlemen going into the shady woods to picnic upon soft sprigs and bashful anemones, or strolling to

> A bank I know whereon the wild thyme blows,
> Where ox-lips and the nodding violet grows,
> Quite over-canopied with lush woodbine,
> With sweet musk-roses, and with eglantine;

sitting down to supper on these dainties, surrounded by sweet tinkling bells of lowing bo-ohs and bleating ba-bas. Burglars and forgers, judges and juries, will be things of the past.

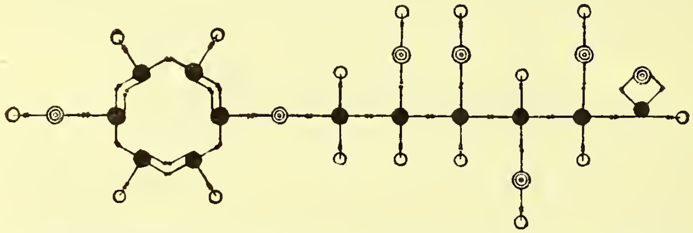
Dextrin is produced from starch by treating it with dilute acids. It is a mixture of several isomeric substances (*amylo-*, *erythro-*, and *achroo-dextrin*). By further action of the acid it is converted into dextrose, and by diastase into maltose. Commercial dextrin is mainly erythro-dextrin, but mixed besides with starch and sugar. It is a constituent of nearly all sorts of 'infant's food' on account of its easy digestibility. According to investigations on the molecular weight of carbohydrates by Raoult's method (p. 279), dextrin has the formula $(C_{12}H_{20}O_{10})_6$ (*Trans. Chem. Soc.* 1888, p. 610).

# GLUCOSIDES

Glucosides are ethers formed, as a rule, from glucoses, generally dextrose (fig. 616, p. 153) and a phenol (or phenol-alcohol, alcohol-phenol-ether, &c.) through their alcoholic hydroxyls joining in the regular ether fashion by dropping a molecule of water; they occur in the vegetable world, and are split up into their components by ferments, dilute acids, or alkalies. There are about a hundred of them known, but the structures of very few have been ascertained.

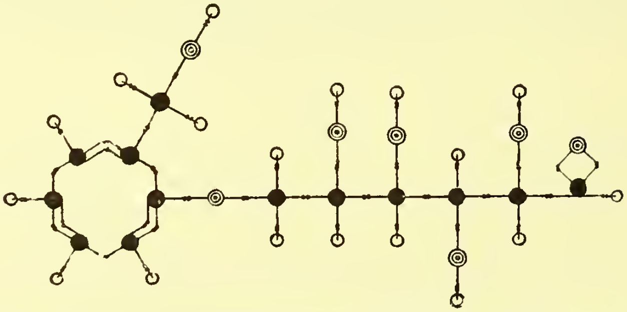
Some of these are—

Fig. 634



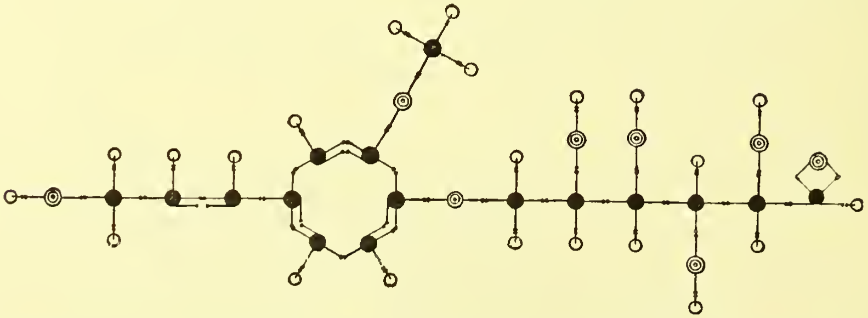
Arbutin, $C_{12}H_{16}O_7$; m.p. 165°; formed from *hydroquinone* (fig. 420, p. 92) and *dextrose*; occurs in the leaves of the bear-berry (*Arbutus uva ursi*); is used in affections of the bladder and kidneys

Fig. 635



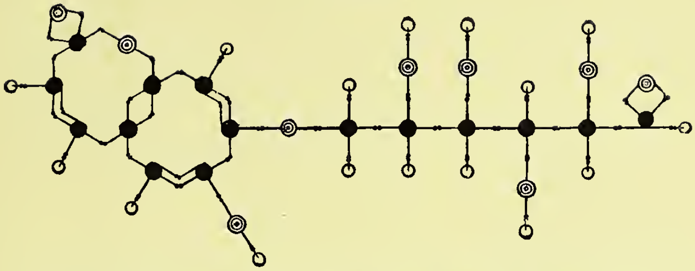
Salicin, $C_{13}H_{18}O_7$; m.p. 201°; formed from *saligenin* (fig. 461, p. 106) and *dextrose*; is present in all species of salix, particularly in *S. helix*, *S. pentandra*, and *S. præcox*, also in *castorcum*; has been used in influenza

Fig. 636



Coniferin, $C_{16}H_{22}O_8$; m.p. 185°; formed from *coniferyl alcohol* (fig. 511, p. 123) and *dextrose*; occurs in the cambial sap of *Coniferæ*

Fig. 637



Æsculin, $C_{15}H_{16}O_9$; m.p. 160°, decomp.; formed from a compound (*æsculetin*) which we have not yet had occasion to discuss, being an ether-formation of an aromatic acid (fig. 836, p. 222) and dextrose; occurs in the bark of the horse-chestnut (*Æsculus hippocastanum*); used for neuralgia

## Future Nomenclature of Aldehydes and Ketones

The rules laid down by the Congress are beautifully simple. For aldehydes the suffix *-al*, and for ketones the suffix *-one*, are added to the name of the hydrocarbon from which they may be considered derived; di- and tri-ketones take the suffixes *-dione* and *-trione*.

Examples of the application of these rules are :—

| *Old Nomenclature* | | | *New Nomenclature* |
|---|---|---|---|
| Formic aldehyde | (fig. 533, p. 130) | = | Methanal |
| Acetic-aldehyde | (fig. 538, p. 131) | = | Ethanal |
| Butyr-aldehyde | (fig. 543, p. 132) | = | Butanal |
| Acroleïn | (fig. 546, p. 132) | = | Propenal |
| Croton-aldehyde | (fig. 549, p. 133) | = | 2 Butenal |
| Geranial | (fig. 553, p. 133) | = | 2 : 6 Dimethyl-octa-4 : 6 dienal |
| Glycollic aldehyde | (fig. 556, p. 135) | = | Ethanolal |
| Erythrose | (fig. 558, p. 135) | = | Butanetriolal |
| Acetone | (fig. 566, p. 138) | = | Propanone |
| Mesityloxide | (fig. 568, p. 138) | = | 2 Methyl-pent-2 ene-4 one |
| Phorone | (fig. 572, p. 139) | = | 2 : 6 Dimethyl-hept-2 : 5 ene-4 one |
| Di-acetyl | (fig. 576, p. 140) | = | Butandione |
| Acetonyl-acetone | (fig. 578, p. 140) | = | Hexane-2 : 5 dione |
| Grape sugar | (fig. 616, p. 153) | = | Hexane-pentolal |
| Levulose | (fig. 620, p. 153) | = | Hexane-pentol-2 one |

Aldehyde-radicals formed by removal of a hydrogen not belonging to the aldehyde-link receive the suffix *-ylal* added to the name of the corresponding hydrocarbon.

Cyclo-compounds are, as already mentioned, not yet provided for.

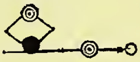
# PART VI.

# Oxygen Compounds

## ACIDS

# Reaction of Hydrogen-peroxide on Aldehydes and Ketones

## ACIDS

*Index,*  *Chemical symbol,* COOH (carboxyl).

### FORMATION

We have seen the hydrocarbons oxidised by hydrogen-peroxide to alcohols, alcohols to aldehydes and ketones, and we shall now see how these latter compounds through the further action of hydrogen-peroxide are transformed into a series of new compounds called acids.

The process is a very simple one as regards aldehydes; the hydrogen-atom fixed on the carbonyl group is removed and a hydroxyl takes its place. We will illustrate the process by choosing methyl- and ethyl-aldehydes as examples (figs. 533 and 538, pp. 130 and 131):

Fig. 638

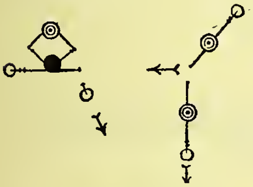
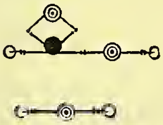


Fig. 639



Methyl-aldehyde + hydrogen-peroxide = Formic acid + water

Fig. 640

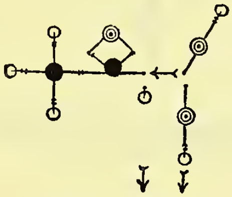
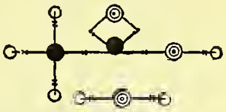


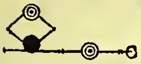
Fig. 641



Ethyl-aldehyde + hydrogen-peroxide = Acetic acid + water

One thing must be noticeable in the figures of the acids, viz. that they have the figure

Fig. 642

 in common. This figure is characteristic of *all* acids and is termed carboxyl.

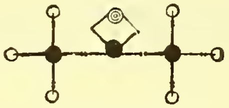
The four valencies of the carbon-atom in carboxyl group are disposed of in this way: two are employed in holding the oxygen-atom, a third is engaged by the hydroxyl, the three together showing that the molecule of which they constitute one part has the character of an acid; the fourth valency is joined to something else, in most cases an alcohol radical or a phenyl-group, indicating what sort of an acid it is.

What is required of a carbon-atom capable of forming an acid is, therefore, three valencies disposable, two for the oxygen and one for the hydroxyl. If one of these three valencies is bound to a carbon-atom it must tear itself free from that bondage, breaking up the chain into two fragments, or, in the case of a closed chain, the ring will be opened and one or more straight chains formed. It follows from this that an acid can only be formed from aldehydes, never from ketones without disturbing the chain; and because aldehydes are formed from primary alcohols, and ketones from secondary, acids cannot be derived from any but primary alcohols without splitting the chain.[1]

We have seen the simple process taking place in the case of an aldehyde; we will now show the splitting of a ketone, di-methyl-ketone, for instance (fig. 566, p. 138).

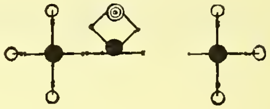
In the first instance it breaks up into two fragments in order to give a third valency free to the carbonyl-link:

Fig. 643



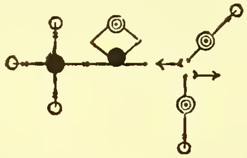
Di-methyl-ketone

Fig. 644



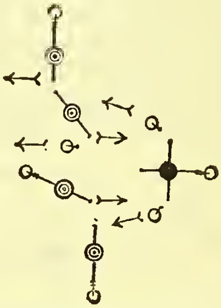
By this breaking up, two groups are formed, both of which are fit for the operation of hydrogen-peroxide, which consequently acts by making acids of both. Three molecules of hydrogen-peroxide are required for the purpose of the process, which is effected in the following manner:

Fig. 645



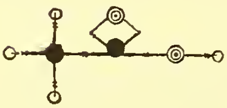
The left part of di-methyl-ketone + one molecule of hydrogen-peroxide

Fig. 646



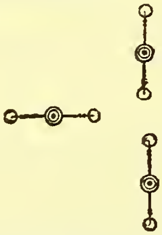
The right part of di-methyl-ketone + two molecules of hydrogen-peroxide

Fig. 647



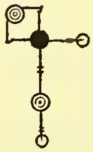
Acetic acid

Fig. 648



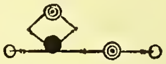
Three molecules of water

Fig. 649



or

Fig. 650



Formic acid

The final products being acetic acid, water, and formic acid

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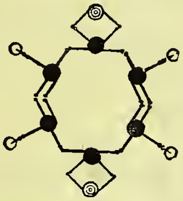
[1] For this reason phenols, being either secondary or tertiary alcohols, cannot form acids without breaking the chain; consequently acids with a phenyl-group (aromatic acids) are not simple but compound acids, which will have to be mentioned afterwards.

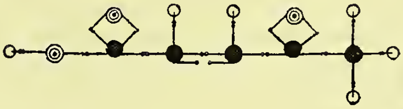
Ring-formed compounds are broken up in the most varied manner. Here is an example:

FIG. 651



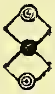
=

FIG. 652



+

FIG. 653



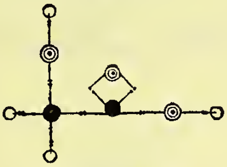
Quinone (fig. 584, p. 142) β-Acetyl-acrylic acid [1] + Carbon-dioxide

As the simple acids produced by the breaking up of secondary or tertiary alcohols, and of ring-formed compounds, are the same as those we get from primary alcohols, we need only discuss the derivation of acids from the latter sort of alcohols. The compound acids will be treated in a subsequent part.

There are many more acids than alcohols because we have alcohols with more than one hydroxyl, and in such the carboxyl may be formed from every carbon-atom satisfying the conditions stated above.

Thus *glycol* (fig. 364, p. 76) can give us two acids:

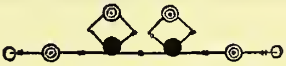
FIG. 654



Glycollic acid

and

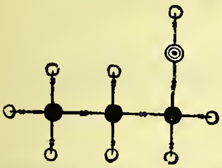
FIG. 655



Oxalic acid

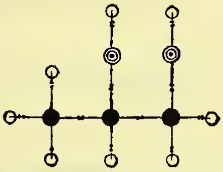
The under-mentioned four primary, or partly primary, alcohols are derived from *propane* (fig. 18, p. 8):

FIG. 656



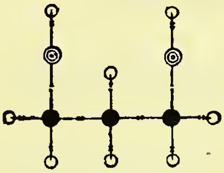
Primary propyl-alcohol (fig. 338, p. 70)

FIG. 657



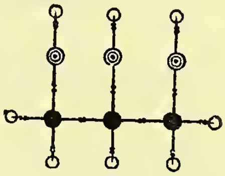
α-Propylene-glycol; primary-secondary (fig. 366, p. 77)

FIG. 658



β-Propylene-glycol; di-primary (fig. 367, p. 77)

FIG. 659



Glycerol (glycerin); di-primary-secondary (fig. 375, p. 78)

The carbon-atoms are individualised by letters from the Greek alphabet: the atom next to the carboxyl (being or to be) is indexed α-, and the others β-, γ-, δ-, ε-, &c., according to order; the first and the last ones, i.e. the carboxyl and the opposite end-link in *long* chains, are generally termed respectively ω- and ω′ (*vide* p. 36).

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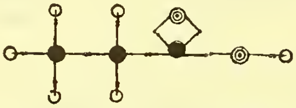
[1] In the actual experiment, proving the correctness of the theory, a quinone was acted upon in which three hydrogens were replaced by chlorine, and the product of oxidation was not acetyl-acrylic acid, but trichlor-acetyl-acrylic acid (*Ann.* ccxxi. p. 230). For our purpose that makes no difference.

From these four alcohols six different acids are derived:

From *propyl-alcohol* one acid:

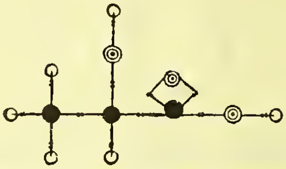
From *a-propylene-glycol* one acid:

Fig. 660



Propionic acid; monobasic (monatomic)

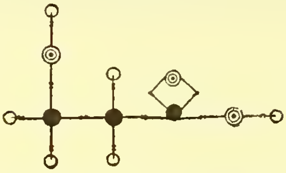
Fig. 661



Ethylidene-lactic acid; monohydroxy-monobasic (diatomic)

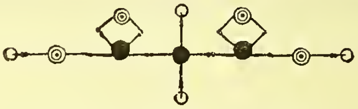
From *β-propylene-glycol* two acids:

Fig. 662



Ethylene-lactic acid; monohydroxy-monobasic (diatomic)

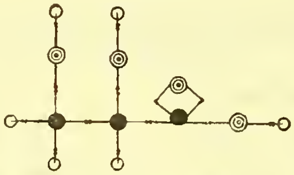
Fig. 663



Malonic acid; dibasic (diatomic)

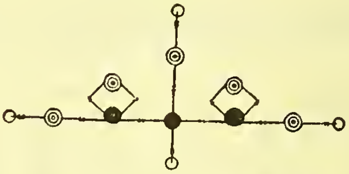
From *glycerol* two acids:

Fig. 664



Glyceric acid; dihydroxy-monobasic (triatomic)

Fig. 665



Tartronic acid; monohydroxy-dibasic (triatomic)

From *propane* no less than four alcohols and six acids are thus derived. When we come to the higher homologues of the hydrocarbons the theoretical number increases vastly; there are seven *heptylic acids*, $C_7H_{14}O_2$, thirty-eight *octylic*, $C_8H_{16}O_2$, and 507 *undecylic acids* &c. possible; and besides these, hydroxylated acids, acids with aldehydes, ketones, &c., in their structures, all derivable from their respective hydrocarbons. Consequently we must classify.

We have three points assisting us in bringing the confusion into order.

First we classify them according to the hydrocarbons of which they may be considered derivatives.

Next we subdivide them according to the number of carboxyls they contain.

And lastly they are distinguished by the number of hydroxyls (if any).

Acids have many qualities in common, but there is one more important and prominent than the others, and that is their capability of, or rather avidity for, exchanging the hydrogen in their carboxyl for other things, but specially for metals. It is the same peculiar feature we have found, though not so pronounced, amongst the properties of phenols (phenolates, p. 109), and in a still lesser degree in alcohols (*l. c.*), yet sufficient in the phenols to have given to some of them the name of acids (*e.g.*, carbolic acid). When a metal has substituted all such hydrogen-atoms the acid has lost all its acid properties, the new compound is a neutral one, or, as the chemists term it, a salt. An acid can receive as many atoms of a metal as it has carboxyls, and as we call a metal a base, the acids are said to be monobasic, dibasic, &c., according to the number of carboxyls whose hydrogen-atoms may be exchanged for metallic atoms. The property of exchanging the hydrogen for metals is called their basicity. Higher basicity than hexabasic acids' is not known

By the number of hydroxyls which acids contain besides the hydroxyl of the carboxyl, they are distinguished as mono-hydroxy-, di-hydroxy-, &c., frequently also as monoxy-, dioxy-, &c.

A great many chemists refer to the number of hydroxyls of the alcohol from which the acid is derived, and as they use the designation 'atomic' for alcohols (*vide* p. 68), they retain the same for acids. Accordingly an acid with one carboxyl and three hydroxyls, another with two carboxyls and two hydroxyls, a third with three carboxyls and one hydroxyl, would all be tetra-atomic, because the original alcohol had four hydroxyls.

All these designations are appended to the examples above, but I do not intend to apply the designation of atomicity to acids, partly because the classification must be altered, and, in my opinion, not to the advantage of the general view of the classes and their connections; partly because it is not so expressive as the other one; and finally because it is not in harmony with the nomenclature, present and probably future.

In the tables on the next pages the acids are arranged according to this principle:

The monobasic fatty acids proper, i.e. free from hydroxyls, are arranged in a horizontal row at the foot of the table I*a* and at the top of I*b*, commencing with formic acid and propionic acid respectively.

These I have termed fundamental acids.

All other acids may be considered, and often are actually, formed from these and their isomers by

1. Leaving their general structure and their linkage undisturbed, but substituting methyls by (i.e. oxidising them to) carboxyls. Six classes (as far as we at present know) are thus formed with one, two, three, four, five, or six carboxyls. Only the three first are represented on Table I*a*, arranged consecutively from fundamental fatty acids towards the top of the page. These classes are each subdivided according to the number of hydroxyls replacing hydrogen-atoms.

All hydroxy-acids are printed in italics. The whole of this division is termed saturated aliphatic acids (derivable from the saturated hydrocarbons).

2. Leaving their general structure undisturbed, but creating double or triple bonds by removal of hydrogen-atoms in pairs, just as we did with hydrocarbons. In this way seven classes are formed—with one, two, three, or four double bonds, and with one, two, or four triple bonds. These classes, except the last three, are arranged in Table I*b*, from the fundamental acids downwards, in the order in which they are mentioned here. Each class is divided, as above, with regard to carboxyls, and subdivided according to the number of substituting hydroxyls: these last subdivisions are also printed in italics. The whole division is termed unsaturated aliphatic acids.

For the better comprehension of the structural connection between all acids, facilitating a comparison between them, and showing at a glance what they have in common, and in what they differ, examples of the saturated aliphatic acids including the three classes shut out from Table I*a* are illustrated in Table II.

The same has been done with the unsaturated acids with one double bond, in Table III.; those with more than one double bond are so few, and their constitution so little known, that Table I*a* and the specification following will suffice; on Table IV. those acids with triple bonds left out from Table I*b* are scheduled.

The pictorial examples have been selected exclusively for their instructiveness; they do not necessarily all belong to the better known compounds, and they illustrate of course only a representative of each division, which division often contains a series of homologues and a number of isomers of each homologue (p. 12).

The four-, five-, and six-basic saturated acids in Table II., and the acetylene acids in Table IV., are mere curiosities which the eye of but very few chemists indeed has had the good fortune to fall upon. Some of them are not even known in the free state, but theoretically they are highly interesting.

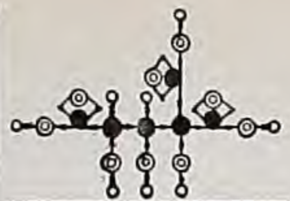
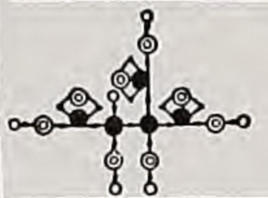
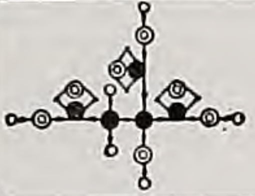
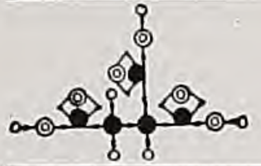
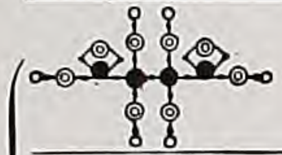
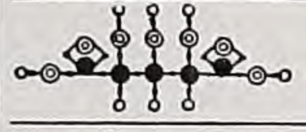
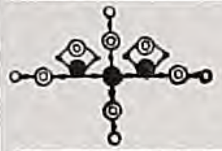
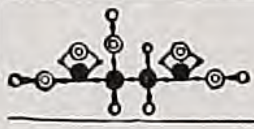
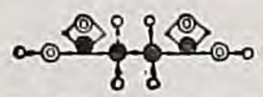
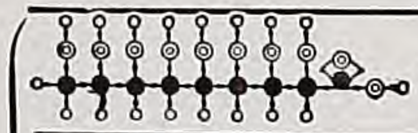
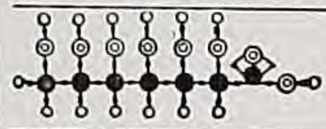
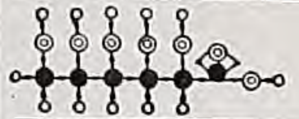
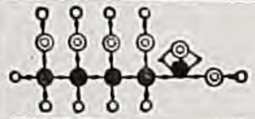
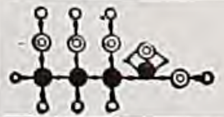
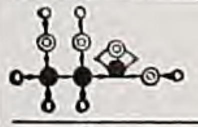
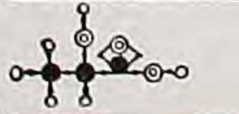
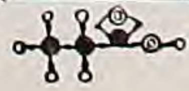
An index to Tables I*a* and I*b* will be found on p. 171.

To follow p. 170

# TABLE Ia.

## SATURATED ALIPHATIC ACIDS

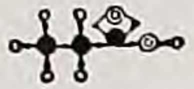
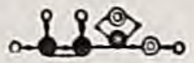
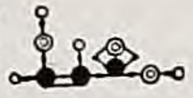
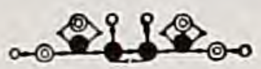
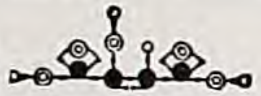
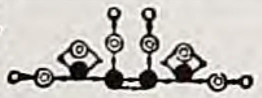
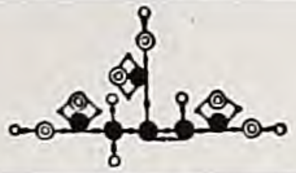
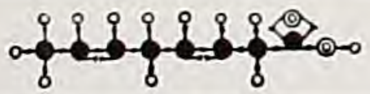
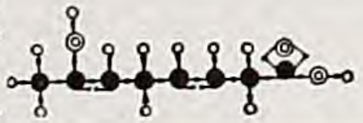
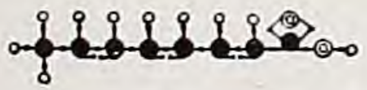
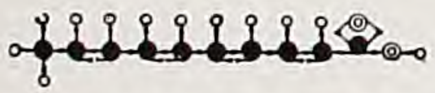
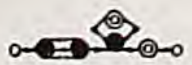
### METHANE DERIVATIVES

| | | | | | a | b | c | d | e | f | g | h | i | j | k | l | m | n | o | p | q | r | s |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Tribasic | Tri-hydroxylic |  | $C_nH_{2n-4}O_9$ | 1 | | | | | | *Dihydroxy-iso-citric*<br>$C_6H_8O_9$ | | | | | | | | | | | | | |
| | Di-hydroxylic |  | $C_nH_{2n-4}O_8$ | 2 | | | | | *Desoxalic*<br>$C_5H_6O_8$ | *Hydroxy-citric*<br>$C_6H_8O_8$ | | | | | | | | | | | | | |
| | Mono-hydroxylic |  | $C_nH_{2n-4}O_7$ | 3 | | | | | | *Citric*<br>$C_6H_8O_7$ | | | | | | | | | | | | | |
| | |  | $C_nH_{2n-4}O_6$ | 4 | | | | | Ethenyl-tri-carboxylic<br>$C_5H_6O_6$ | Tri-carballylic<br>$C_6H_8O_6$ | | Pentane-tri-carboxylic<br>$C_8H_{12}O_6$ | | | | | | | | | | | |
| Dibasic | Tetra-hydroxylic |  | $C_nH_{2n-2}O_8$ | 5 | | | | *Dihydroxy-tartaric*<br>$C_4H_6O_8$ | | *Saccharic*<br>$C_6H_{10}O_8$ | | | | | | | | | | | | | |
| | Tri-hydroxylic |  | $C_nH_{2n-2}O_7$ | 6 | | | | | *Aposorbic*<br>$C_5H_8O_7$ | *Trihydroxy-adipic*<br>$C_6H_{10}O_7$ | | | | | | | | | | | | | |
| | Di-hydroxylic |  | $C_nH_{2n-2}O_6$ | 7 | | | *Mesoxalic*<br>$C_3H_4O_6$ | *Tartaric*<br>$C_4H_6O_6$ | | *Dihydroxy-adipic*<br>$C_6H_{10}O_6$ | | | | | | | | | | | | | |
| | Mono-hydroxylic |  | $C_nH_{2n-2}O_5$ | 8 | | | *Tartronic*<br>$C_3H_4O_5$ | *Malic*<br>$C_4H_6O_5$ | *Hydroxy-glutaric*<br>$C_5H_8O_5$ | *Methyl-hydroxy-glutaric*<br>$C_6H_{10}O_5$ | *Diaterebic*<br>$C_7H_{12}O_5$ | *Hydroxy-suberic*<br>$C_8H_{14}O_5$ | | | | | | | | | | | |
| | |  | $C_nH_{2n-2}O_4$ | 9 | | Oxalic<br>$C_2H_2O_4$ | Malonic<br>$C_3H_4O_4$ | Succinic<br>$C_4H_6O_4$ | Pyrotartaric<br>$C_5H_8O_4$ | Adipic<br>$C_6H_{10}O_4$ | Pimelic<br>$C_7H_{12}O_4$ | Suberic<br>$C_8H_{14}O_4$ | Azelaïc<br>$C_9H_{16}O_4$ | Sebacic<br>$C_{10}H_{18}O_4$ | | Brassylic<br>$C_{13}H_{24}O_4$ | | | Roccellic<br>$C_{17}H_{32}O_4$ | | | | |
| Monobasic | Octa-hydroxylic |  | $C_nH_{2n}O_{10}$ | 10 | | | | | | | | | | | | | | | *Octa-hydroxy-margaric*<br>$C_{17}H_{34}O_{10}$ | | | | |
| | Hexa-hydroxylic |  | $C_nH_{2n}O_8$ | 11 | | | | | | *Tri-glycollic ?*<br>$C_6H_{12}O_8$ | *Carbo-gluconic ?*<br>$C_7H_{14}O_8$ | | | | | | | | | *Hexa-hydroxy-stearic*<br>$C_{18}H_{36}O_8$ | | | |
| | Penta-hydroxylic |  | $C_nH_{2n}O_7$ | 12 | | | | | | *Gluconic*<br>$C_6H_{12}O_7$ | | | | | | | | | | | | | |
| | Tetra-hydroxylic |  | $C_nH_{2n}O_6$ | 13 | | | | | *Arabonic*<br>$C_5H_{10}O_6$ | *Saccharinic*<br>$C_6H_{12}O_6$ | | | | | | | | | | *Tetra-hydroxy-stearic*<br>$C_{18}H_{36}O_6$ | | | |
| | Tri-hydroxylic |  | $C_nH_{2n}O_5$ | 14 | | | | *Erythro-glucinic*<br>$C_4H_8O_5$ | | | | | | | | | | | | *Trihydroxy-stearic*<br>$C_{18}H_{36}O_5$ | | | |
| | Di-hydroxylic |  | $C_nH_{2n}O_4$ | 15 | | *Glyoxalic*<br>$C_2H_4O_4$ | *Glyceric*<br>$C_3H_6O_4$ | *Dihydroxy-butyric*<br>$C_4H_8O_4$ | *Dihydroxy-valeric*<br>$C_5H_{10}O_4$ | *Dihydroxy-caproïc*<br>$C_6H_{12}O_4$ | *Dihydroxy-heptylic*<br>$C_7H_{14}O_4$ | | | | *Dihydroxy-undecylic*<br>$C_{11}H_{22}O_4$ | | | | | *Dihydroxy-stearic*<br>$C_{18}H_{36}O_4$ | *Dihydroxy-jecoleïc*<br>$C_{19}H_{38}O_4$ | | *Iso-dihydroxy-behenic*<br>$C_{22}H_{44}O_4$ |
| | Mono-hydroxylic |  | $C_nH_{2n}O_3$ | 16 | *Carbonic*<br>$CH_2O_3$ | *Glycollic*<br>$C_2H_4O_3$ | *Hydroxy-propionic*<br>$C_3H_6O_3$ | *Hydroxy-butyric*<br>$C_4H_8O_3$ | *Hydroxy-valeric*<br>$C_5H_{10}O_3$ | *Hydroxy-caproïc*<br>$C_6H_{12}O_3$ | *Hydroxy-œnanthylic*<br>$C_7H_{14}O_3$ | *Hydroxy-caprylic*<br>$C_8H_{16}O_3$ | *Hydroxy-nonylic*<br>$C_9H_{18}O_3$ | *Hydroxy-decylic*<br>$C_{10}H_{20}O_3$ | | *Di-iso-amyl-oxalic*<br>$C_{12}H_{24}O_3$ | *Hydroxy-myristic*<br>$C_{14}H_{28}O_3$ | *Hydroxy-palmitic*<br>$C_{16}H_{32}O_3$ | *Hydroxy-margaric*<br>$C_{17}H_{34}O_3$ | *Hydroxy-stearic*<br>$C_{18}H_{36}O_3$ | | | |
| | |  FUNDAMENTAL ACIDS | $C_nH_{2n}O_2$ | 17 | **Formic**<br>$CH_2O_2$ | **Acetic**<br>$C_2H_4O_2$ | **Propionic**<br>$C_3H_6O_2$ | **Butyric**<br>$C_4H_8O_2$ | **Valeric**<br>$C_5H_{10}O_2$ | **Caproïc**<br>$C_6H_{12}O_2$ | **Œnanthylic**<br>$C_7H_{14}O_2$ | **Caprylic**<br>$C_8H_{16}O_2$ | **Pelargonic**<br>$C_9H_{18}O_2$ | **Capric**<br>$C_{10}H_{20}O_2$ | **Undecylic**<br>$C_{11}H_{22}O_2$ | **Lauric**<br>$C_{12}H_{24}O_2$ | **Myristic**<br>$C_{14}H_{28}O_2$ | **Palmitic**<br>$C_{16}H_{32}O_2$ | **Margaric**<br>$C_{17}H_{34}O_2$ | **Stearic**<br>$C_{18}H_{36}O_2$ | **Nondecylic**<br>$C_{19}H_{38}O_2$ | **Arachidic**<br>$C_{20}H_{40}O_2$ | **Behenic**<br>$C_{22}H_{44}O_2$ |

# TABLE I*b*.

## UNSATURATED ALIPHATIC ACIDS

DERIVATIVES FROM

| | | | | | | *c* | *d* | *e* | *f* | *g* | *h* | *i* | *j* | *k* | *n* | *o* | *p* | *q* | *s* | *t* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| FUNDAMENTAL ACIDS | | |  | $C_nH_{2n}O_2$ | **17** | **Propionic**<br>$C_3H_6O_2$ | **Butyric**<br>$C_4H_8O_2$ | **Valeric**<br>$C_5H_{10}O_2$ | **Caproïc**<br>$C_6H_{12}O_2$ | **Œnanthylic**<br>$C_7H_{14}O_2$ | **Caprylic**<br>$C_8H_{16}O_2$ | **Pelargonic**<br>$C_9H_{18}O_2$ | **Capric**<br>$C_{10}H_{20}O_2$ | **Undecylic**<br>$C_{11}H_{22}O_2$ | **Palmitic**<br>$C_{16}H_{32}O_2$ | **Margaric**<br>$C_{17}H_{34}O_2$ | **Stearic**<br>$C_{18}H_{36}O_2$ | **Nondecylic**<br>$C_{19}H_{38}O_2$ | **Behenic**<br>$C_{22}H_{44}O_2$ | **Lignosceric**<br>$C_{24}H_{48}O_2$ |
| ETHYLENE | Monobasic | |  | $C_nH_{2n-2}O_2$ | **18** | Acrylic<br>$C_3H_4O_2$ | Crotonic<br>$C_4H_6O_2$ | Angelic<br>$C_5H_8O_2$ | Pyroterebic<br>$C_6H_{10}O_2$ | Teracrylic<br>$C_7H_{12}O_2$ | Suberonic<br>$C_8H_{14}O_2$ | Nonylenic<br>$C_9H_{16}O_2$ | Decylenic<br>$C_{10}H_{18}O_2$ | Undecylenic<br>$C_{11}H_{20}O_2$ | Hypogæïc<br>$C_{16}H_{30}O_2$ | | Oleïc<br>$C_{18}H_{34}O_2$ | Jecoleïc<br>$C_{19}H_{36}O_2$ | Erucic<br>$C_{22}H_{42}O_2$ | |
| | | Mono-hydroxylic |  | $C_nH_{2n-2}O_3$ | **19** | | *Hydroxy-crotonic*<br>$C_4H_6O_3$ | | | *Mesitonic*<br>$C_7H_{12}O_3$ | | | | | *Hydroxy-hypogæïc*<br>$C_{16}H_{30}O_3$ | | *Ricinoleïc*<br>$C_{18}H_{34}O_3$ | | *Hydroxy-erucic*<br>$C_{22}H_{42}O_3$ | |
| | Dibasic | |  | $C_nH_{2n-4}O_4$ | **20** | | Maleïc<br>$C_4H_4O_4$ | Itaconic<br>$C_5H_6O_4$ | Hydromuconic<br>$C_6H_8O_4$ | Allyl-succinic<br>$C_7H_{10}O_4$ | Xeronic<br>$C_8H_{12}O_4$ | | | | | | | | | |
| | | Mono-hydroxylic |  | $C_nH_{2n-4}O_5$ | **21** | | | *Hydroxy-itaconic*<br>$C_5H_6O_5$ | *Hydroxy-hydro-muconic*<br>$C_6H_8O_5$ | | | | | | | | | | | |
| | | Di-hydroxylic |  | $C_nH_{2n-4}O_6$ | **22** | | *Dihydroxy-maleïc*<br>$C_4H_4O_6$ | | | | | | | | | | | | | |
| | Tribasic | |  | $C_nH_{2n-6}O_6$ | **23** | | | | Aconitic<br>$C_6H_6O_6$ | | | | | | | | | | | |
| DI-ETHYLENE | Monobasic | |  | $C_nH_{2n-4}O_2$ | **24** | | | | Sorbic<br>$C_6H_8O_2$ | | Diallyl-acetic<br>$C_8H_{12}O_2$ | | | | | Elæo-margaric<br>$C_{17}H_{30}O_2$ | Linolic<br>$C_{18}H_{32}O_2$ | | | |
| | | Mono-hydroxylic |  | $C_nH_{2n-4}O_3$ | **25** | | | | | | *Diallyl-oxalic*<br>$C_8H_{12}O_3$ | | | | | | | | | |
| TRI-ETHYLENE | Monobasic | |  | $C_nH_{2n-6}O_2$ | **26** | | | | | | | | | | | | Linolenic<br>$C_{18}H_{30}O_2$ | | | |
| TETRA-ETHYLENE | Monobasic | |  | $C_nH_{2n-8}O_2$ | **27** | | | | | | | | | | | Therapic<br>$C_{17}H_{26}O_2$ | | | | |
| ACETYLENE | Monobasic | |  | $C_nH_{2n-4}O_2$ | **28** | Propiolic<br>$C_3H_2O_2$ | Tetrolic<br>$C_4H_4O_2$ | | | Butyl-acetylene-carboxylic<br>$C_7H_{10}O_2$ | | Lauronolic<br>$C_9H_{14}O_2$ | | Undecolic<br>$C_{11}H_{18}O_2$ | Palmitolic<br>$C_{16}H_{28}O_2$ | | Stearolic<br>$C_{18}H_{32}O_2$ | | Behenolic<br>$C_{22}H_{40}O_2$ | |

# INDEX OF ALIPHATIC ACIDS ON TABLES I*a* AND I*b*

Acetic . . . . . 17—*b*
Aconitic . . . . 23—*f*
Acrylic . . . . . 18—*c*
Adipic . . . . . 9—*f*
Allyl-succinic . . . 20—*g*
Angelic . . . . 18—*e*
Aposorbic . . . . 6—*e*
Arabonic . . . . 13—*e*
Arachidic . . . . 17—*r*
Azelaïc . . . . 9—*i*

Behenic . . . . . 17—*s*
Behenolic . . . . 28—*s*
Brassylic . . . . 9—*lm*
Butyl-acetylene-carboxylic . 28—*g*
Butyric . . . . 17—*d*

Capric . . . . . 17—*j*
Caproïc . . . . . 17—*f*
Caprylic . . . . . 17—*h*
Carbo-gluconic . . . 11—*g*
Carbonic . . . . . 16—*a*
Citric . . . . . . 3—*f*
Crotonic . . . . 18—*d*

Decylenic . . . . 18—*j*
Desoxalic . . . . . 2—*e*
Di-allyl-acetic . . . 24—*h*
„ „ oxalic . . . 25—*h*
Diaterebic . . . . . 8—*g*
Di-hydroxy-adipic . . 7—*f*
„ „ butyric . . 15—*d*
„ „ caproïc . . 15—*f*
„ „ heptylic . . 15—*g*
„ „ iso-citric . . 1—*f*
„ „ jecoleïc . . 15—*q*
„ „ maleïc . . 22—*d*
„ „ stearic . . 15—*p*
„ „ tartaric . . 5—*d*
„ „ undecylic . . 15—*k*
„ „ valeric . . 15—*e*
Di-iso-amyl-oxalic . . 16—*l*

Elæo-margaric . . . 24—o
Erucic . . . . . 18—*s*
Erythro-glucinic . . . 14—*d*
Ethenyl-tri-carboxylic . . 4—*e*

Formic . . . . . 17—*a*

Gluconic . . . . . 12—*f*
Glyceric . . . . . 15—*c*
Glycollic . . . . . 16—*b*
Glyoxalic . . . . . 15—*b*

Hexa-hydroxy-stearic . . 11—*p*
Hydro-muconic . . . 20—*f*
Hydroxy-butyric . . . 16—*d*
„ caproïc . . . 16—*f*
„ caprylic . . . 16—*h*
„ citric . . . 2—*f*
„ crotonic . . . 19—*d*
„ decylic . . . 16—*j*
„ erucic . . . 19—*s*
„ glutaric . . . 8—*e*
„ hydro-muconic . 21—*f*
„ hypogæïc . . 19—*n*
„ itaconic . . 21—*e*
„ margaric . . 16—o
„ myristic . . 16—*m*
„ nonylic . . . 16—*i*
„ œnanthylic . . 16—*g*
„ palmitic . . 16—*n*
„ propionic . . 16—*c*
„ stearic . . . 16—*p*
„ suberic . . . 8—*h*
„ valeric . . . 16—*e*
Hypogæïc . . . . 18—*n*

Iso-di-hydroxy-behenic . 15—*s*
Itaconic . . . . 20—*e*

Jecoleïc . . . . . 18—*q*

Lauric . . . . . 17—*l*
Lauronolic . . . . 28—*i*
Lignoceric . . . . 17—*t*
Linolenic . . . . . 26—*p*
Linolic . . . . . 24—*p*
Linusic (Hexa-hydroxy-stearic) 11—*p*

Maleïc . . . . . 20—*d*
Malic . . . . . . 8—*d*
Malonic . . . . . 9—*c*
Margaric . . . . . 17—o
Mesitonic . . . . . 19—*g*
Mesoxalic . . . . . 7—*c*
Methyl-hydroxy-glutaric . 8—*f*
Myristic . . . . . 17—*m*

Nondecylic . . . . 17—*q*
Nonylenic . . . . 18—*i*

Octa-hydroxy-margaric . 10—o
Œnanthylic . . . . 17—*g*
Oleïc . . . . . . 18—*p*
Oxalic . . . . . . 9—*b*

Palmitic . . . . . 17—*n*
Palmitolic . . . . 28—*n*
Pelargonic . . . . 17—*i*
Pentane-tri-carboxylic . . 4—*h*
Pimelic . . . . . 9—*g*
Propiolic . . . . . 28—*c*
Propionic . . . . . 17—*c*
Pyrotartaric . . . . 9—*e*
Pyroterebic . . . . 18—*f*

Ricinoleïc . . . . 19—*p*
Roccellic . . . . . 9—o

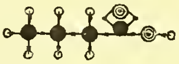
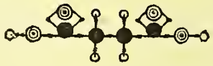
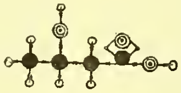
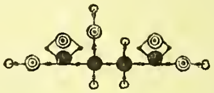
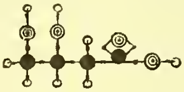
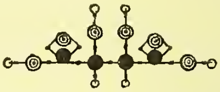
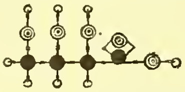
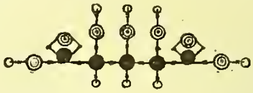
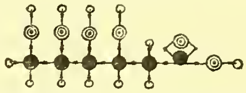
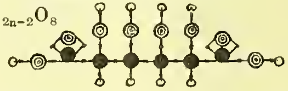
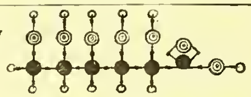
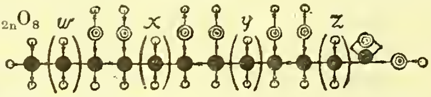
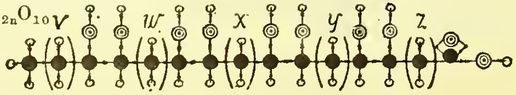
Saccharic . . . . . 5—*f*
Saccharinic . . . . 13—*f*
Sativic (Tetra-hydroxy-stearic) 13—*p*
Sebacic . . . . . 9—*j*
Sorbic . . . . . . 24—*f*
Stearic . . . . . 17—*p*
Stearolic . . . . . 28—*p*
Suberic . . . . . 9—*h*
Suberonic . . . . . 18—*h*
Succinic . . . . . 9—*d*

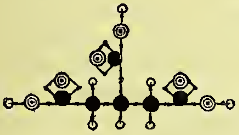
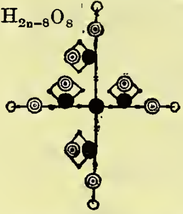
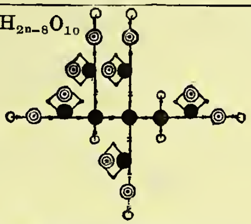
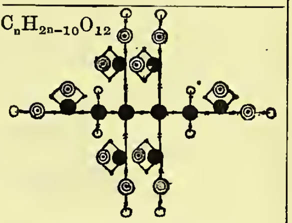
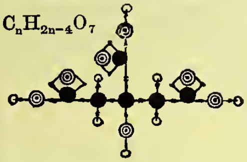
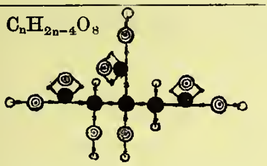
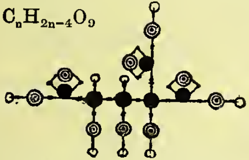
Tartaric . . . . . 7—*d*
Tartronic . . . . . 8—*c*
Teracrylic . . . . 18—*g*
Tetra-hydroxy-stearic . . 13—*p*
Tetrolic . . . . . 28—*d*
Therapic . . . . . 27—o
Tri-carballylic . . . 4—*f*
„ glycollic . . . 11—*f*
„ hydroxy-adipic . . 6—*f*
„ „ stearic . . 14—*p*

Undecolic . . . . 28—*k*
Undecylenic . . . . 18—*k*
Undecylic . . . . 17—*k*

Valeric . . . . . 17—*e*

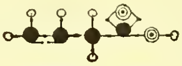
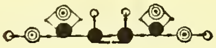
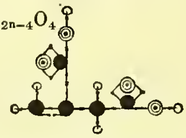
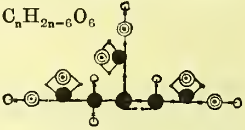
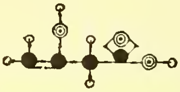
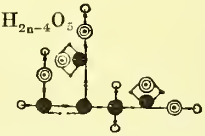
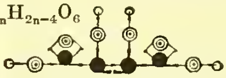
Xeronic . . . . . 20—*h*

| | MONOBASIC | DIBASIC |
|---|---|---|
| | $C_nH_{2n}O_2$  (Monatomic) Butyric Acid<br>$C_4H_8O_2$; b.p. 162°·3 | $C_nH_{2n-2}O_4$  (Diatomic) Succinic Acid<br>$C_4H_6O_4$; m.p. 185° |
| Monhydroxylic . . . | $C_nH_{2n}O_3$  (Diatomic) $\beta$-Hydroxy-Butyric Acid<br>$C_4H_8O_3$; syrupy; decomp. on heating | $C_nH_{2n-2}O_5$  (Triatomic) Malic Acid, $C_4H_6O_5$<br>m.p. 100° |
| Dihydroxylic . . . . | $C_nH_{2n}O_4$  (Triatomic) Dihydroxy-Butyric Acid<br>$C_4H_8O_4$; oily fluid; decomp. on heating | $C_nH_{2n-2}O_6$  (Tetratomic) Tartaric Acid, $C_4H_6O_6$<br>m.p. 135° |
| Trihydroxylic . . . . | $C_nH_{2n}O_5$  (Tetratomic) Erythroglucinic (Erythritic) Acid, $C_4H_8O_5$; deliquescent crystalline mass | $C_nH_{2n-2}O_7$  (Pentatomic) Aposorbic (?) Acid<br>$C_5H_8O_7$; m.p. 110° |
| Tetrahydroxylic . . . | $C_nH_{2n}O_8$  (Pentatomic) Meta-Saccharinic Acid<br>$C_6H_{12}O_6$; m.p. 141° | $C_nH_{2n-2}O_8$  (Hexatomic) Saccharic Acid, $C_6H_{10}O_8$<br>crystals, decomposing on heating |
| Pentahydroxylic . . . | $C_nH_{2n}O_7$  (Hexatomic) Gluconic Acid<br>$C_8H_{12}O_7$; a syrupy liquid | |
| Hexahydroxylic . . . | $C_nH_{2n}O_8$  (Heptatomic) Linusic Acid, $C_{18}H_{36}O_8$; m.p. 203° | |
| Octahydroxylic . . . | $C_nH_{2n}O_{10}$  (Nonatomic) Octahydroxy Margaric Acid, $C_{17}H_{34}O_{10}$; present in Cod Liver Oil that 'repeats'; derived from Therapic Acid | |

| TRIBASIC | TETRABASIC | PENTABASIC | HEXABASIC |
|---|---|---|---|
| $C_nH_{2n-4}O_6$<br><br>(Triatomic) Tricarballylic Acid, $C_6H_8O_8$; m.p. 166° | $C_nH_{2n-8}O_8$<br><br>(Tetratomic) Iso-Allylene Tetra-Carboxylic Acid $C_5H_4O_8$; Crystals | $C_nH_{2n-8}O_{10}$<br><br>(Pentatomic) Propargyl-Penta-Carboxylic Acid, $C_8H_8O_{10}$ not known in free state | $C_nH_{2n-10}O_{12}$<br><br>(Hexatomic) Buton-Hexa-Carboxylic Acid $C_{10}H_{10}O_{12}$; m.p. 56°·5 |
| $C_nH_{2n-4}O_7$<br><br>(Tetratomic) Citric Acid $C_8H_8O_7$; m.p. 153° |  |  |  |
| $C_nH_{2n-4}O_8$<br><br>(Pentatomic) Hydroxy-Citric Acid, $C_8H_8O_8$; crystals |  |  |  |
| $C_nH_{2n-4}O_9$<br><br>(Hexatomic) Dihydroxy Iso-Citric Acid, $C_6H_8O_9$ properties not known |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |

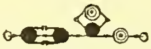
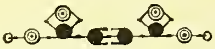
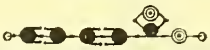
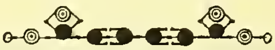
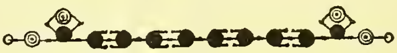
## TABLE III.—UNSATURATED ALIPHATIC ACIDS

*Ethylene Acids*

| | MONOBASIC | DIBASIC | | TRIBASIC |
|---|---|---|---|---|
| | $C_nH_{2n-2}O_2$<br><br>β-Crotonic Acid, $C_4H_6O_2$ | $C_nH_{2n-4}O_4$<br><br>Maleïc Acid, $C_4H_4O_4$ m.p. 130° | $C_nH_{2n-4}O_4$<br><br>Itaconic Acid, $C_5H_6O_4$ m.p. 161° (*vide* fig. 765) | $C_nH_{2n-6}O_6$<br><br>Aconitic Acid, $C_6H_6O_6$ crystals, decomp. by heat |
| Mono-hydroxylic | $C_nH_{2n-2}O_3$<br><br>β-Hydroxy-Crotonic Acid, $C_4H_6O_3$; obtained as an Ether only | | $C_nH_{2n-4}O_5$<br><br>Hydroxy-Itaconic Acid $C_5H_6O_5$; oily liquid decomp. by heat | |
| Di-hydroxylic | | $C_nH_{2n-4}O_6$<br><br>Dihydroxy-Maleïc Acid $C_4H_4O_6$; crystals m.p. not ascertained | | |

## TABLE IV.—UNSATURATED ALIPHATIC ACIDS

*Acetylene Acids*

| MONOBASIC | DIBASIC |
|---|---|
| $C_nH_{2n-4}O_2$<br><br>Acetylene Monocarboxylic Acid, Propiolic Acid, Propargylic Acid, $C_3H_2O_2$; m.p. 6°; b.p. 144° | $C_nH_{2n-6}O_4$<br><br>Acetylene Dicarboxylic Acid, $C_4H_2O_4$; melting at 175° under decomposition |
| $C_nH_{2n-6}O_2$<br><br>Diacetylene Monocarboxylic Acid, $C_5H_2O_2$; explodes violently | $C_nH_{2n-10}O_4$<br><br>Diacetylene Dicarboxylic Acid, $C_6H_2O_4$ very explosive |
| | $C_nH_{2n-18}O_4$<br><br>Tetracetylene Dicarboxylic Acid, $C_{10}H_2O_4$ |

## SPECIFICATION

We can now turn our attention to the structure of a few members of the acids, some possessing a more general, others a more specific therapeutical interest.

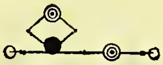
# SATURATED ALIPHATIC ACID SERIES

## Monobasic Acids

### HYDROXYL-FREE (FUNDAMENTAL) ACIDS

The first we meet with is formed from *methyl-alcohol* (fig. 336, p. 69).

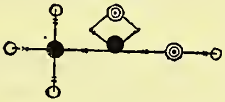
Fig. 666



Formic acid, $CH_2O_2$; m.p. 8°·6, b.p. 100°·8; a powerful corrosive

From *ethyl-alcohol* (fig. 337, p. 70)

Fig. 667

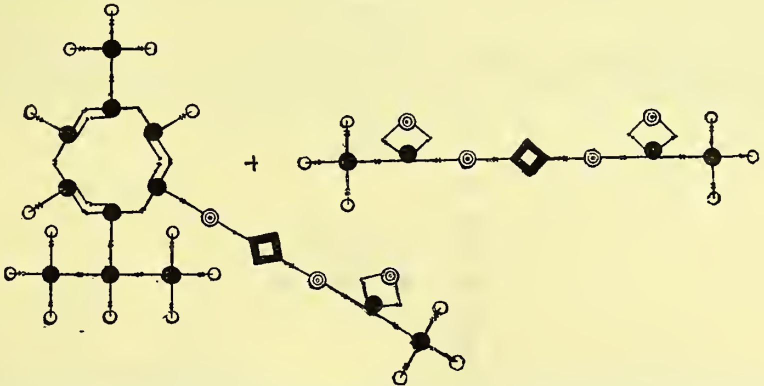


Acetic acid, $C_2H_4O_2$; b.p. 118°

In the cold it solidifies to large crystals melting at 17°: glacial acetic acid. Vinegar contains 3–6 per cent. of this acid.

Acetic acid forms with *thymol* (fig. 434, p. 97) and *mercury* a compound termed mercury thymol-acetate. It consists of two molecules bound together, not by linkage, but by something else, which we call molecular affinity, which, strictly, is but a cloak to cover our ignorance of the nature of the bond. One of these molecules is mercury with thymol on one side and an acetic acid group on the other, and the other molecule is mercury acetate (mercury, being in this case a dyad, binds two acetic acid-groups).

Fig. 668



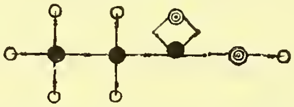
Mercury-thymol-acetate $\left.\begin{matrix}C_{10}H_{13}O\\C_2H_3O_2\end{matrix}\right\}Hg+(C_2H_3O_2)_2Hg=C_{16}H_{22}O_7Hg_2$ (*Merck's Berichte*, Jan. 1893)

A modern syphilis-remedy

The first molecule is, itself, strictly mercury-thymol-acetate, but this name was given to the whole compound before its structure was fully ascertained.

From *primary propyl-alcohol* (fig. 338, p. 70) is derived

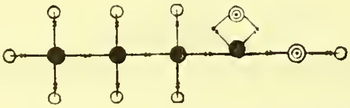
FIG. 669



Propionic acid, $C_3H_6O_2$ ; b.p. 140°

From the two primary *butyl-alcohols* (*vide* normal and iso-butane, figs. 21 and 53, pp. 9 and 13) two acids are derivable:

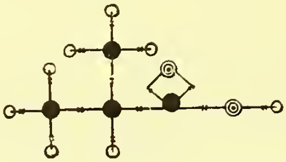
FIG. 670



Normal butyric acid, $C_4H_8O_2$ ; b.p. 162°·5

Has a very unpleasant smell. The free acid is contained in the sweating of the feet and in Limburg cheese; both have their odour from a percentage of this acid; it is present as glyceride in butter (2 per cent.), whence, of course, its name.

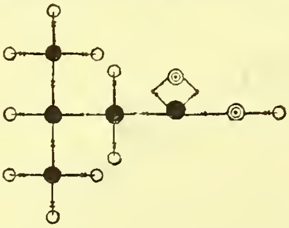
FIG. 671



Iso-butyric acid, $C_4H_8O_2$ ; b.p. 154° ; occurs in carob beans and Roman chamomile oil

From each of the four *primary pentyl-alcohols* (p. 70) an acid has been obtained. Only one of them has found a place in materia medica—that derived from inactive amyl-alcohol (fig. 344, p. 71).

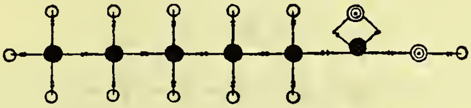
FIG. 672



Inactive valeric-, ordinary valeric-, iso-valeric-, iso-propyl-acetic-, delphinic-, phocenic-, or iso-butyl formic acid, $C_5H_{10}O_2$ ; b.p. 176°·3

From eight possible primary *hexyl-alcohols* seven acids are known. One derived from *normal hexane* (fig. 62, p. 15) or its corresponding alcohol is

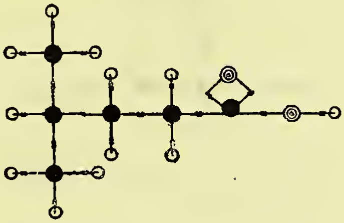
Fig. 673



Normal caproïc acid, $C_6H_{12}O_2$; b.p. 205°

and from *di-methyl-propyl-methane* (fig. 64, p. 15) is derived

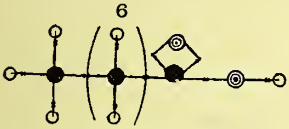
Fig. 674



Iso-butyl-acetic-acid, $C_6H_{12}O_2$; b.p. 200°

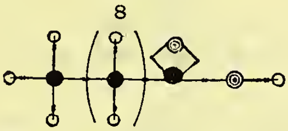
Of the higher homologues may be mentioned

Fig. 675



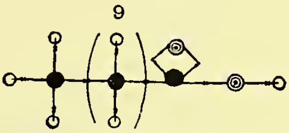
Normal caprylic acid, $C_8H_{16}O_2$;
b.p. 237°

Fig. 676



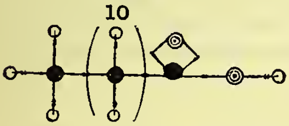
Normal capric acid, $C_{10}H_{20}O_2$;
b.p. 270°

Fig. 677



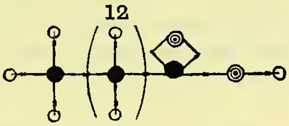
Undecylic acid, $C_{11}H_{22}O_2$;
m.p. 28°

Fig. 678



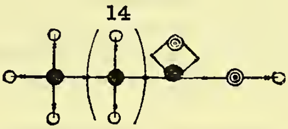
Lauric acid, $C_{12}H_{24}O_2$; m.p. 43°·6

Fig. 679



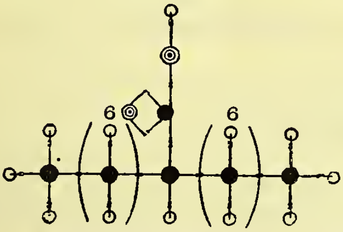
Myristic acid, $C_{14}H_{28}O_2$; m.p. 53°·8

Fig. 680



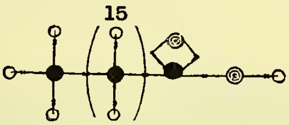
Palmitic acid, $C_{16}H_{32}O_2$; m.p. 62°

Fig. 681



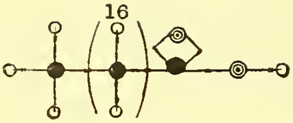
Iso-palmitic acid, di-normal-heptyl-acetic acid; $C_{16}H_{32}O_2$; m.p. 26°

Fig. 682



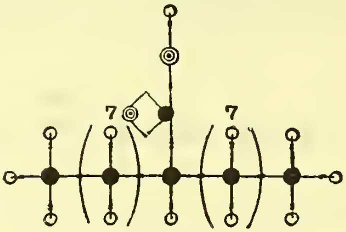
Margaric acid, $C_{17}H_{34}O_2$; m.p. 59°·8

Fig. 683



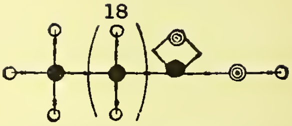
Stearic acid, $C_{18}H_{36}O_2$; m.p. 69°·2

Fig. 684



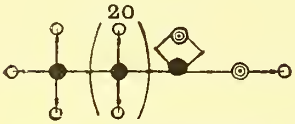
Iso-stearic acid, di-octyl-acetic acid, $C_{18}H_{36}O_2$; m.p. 38°·5

Fig. 685



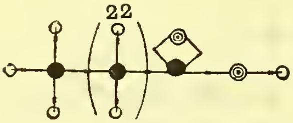
Arachidic acid, $C_{20}H_{40}O_2$; m.p. 75°

Fig. 686



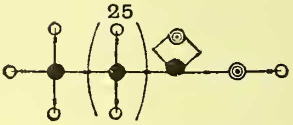
Behenic acid, $C_{22}H_{44}O_2$; m.p. 73°

Fig. 687



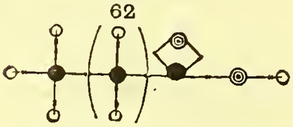
Lignoceric acid, $C_{24}H_{48}O_2$; m.p. 80°·5; isomeric are: gingkoïc acid, paraffinic and carnauba acids

Fig. 688



Cerotic acid, $C_{27}H_{54}O_2$; m.p. 78°; some give it the empirical formula $C_{26}H_{52}O_2$, others say that cerotic acid consists of two different acids, one of which has the formula $C_{34}H_{68}O_2$, m.p. 91° (*Ber.* ix. pp. 278, 1688); cerotic acid is (sometimes, but not always) the chief constituent of beeswax

Fig. 689



Theobromic acid, $C_{64}H_{128}O_2$ (?); m.p. 72°; its existence has been doubted

All of these acids occur in fats of some sort or other—caproïc, caprylic, and capric acids in goat's milk, hence their names. Margaric acid occurs only in one fat, adipocire. The structures of the higher homologues have not been ascertained with any certainty, but their melting-points seem to indicate normal compounds. This criterion is regularly rising with the number of carbon-atoms in the normal acids, yet those with odd numbers and those with even numbers form two distinct series, of which the former have a lower melting-point than the others; for instance

| Number of carbon-atoms . | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Melting-point of even numbers . | 16° | | 30° | | 43° | | 54° | | 62° | | 69° |
| Melting-point of odd numbers . | | 12° | | 28° | | 40° | | 51° | | 60° | |

The melting-point of theobromic acid, 72°, would not indicate a normal, or perhaps not a pure compound.

## HYDROXY-ACIDS

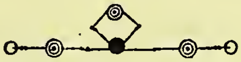
These acids may be considered derivatives from di-acid alcohols (p. 76) by the oxidation of one of their hydroxyl-links into carboxyl (through the intermediate aldehyde-formation), or they may be regarded as derivatives from the fundamental acids, just described, by the substitution of hydroxyls. This latter view of the process will be adopted here, except in cases where a corresponding fundamental acid has not been prepared.

We will therefore illustrate, first, some of the acids derived by the introduction of *one* hydroxyl.

## Mono-hydroxy-acids

In the first of the fundamental acids, *formic acid* (fig. 666, p. 175), a hydrogen-atom is replaceable by hydroxyl, and the hydroxy-acid produced would be

Fig. 690

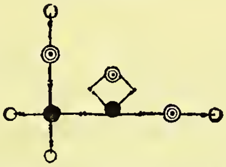


Carbonic acid, $CH_2O_3$; hydroxy-formic acid

The acid has not been isolated, probably on account of the two hydroxyls attached to the same carbon-atom (*vide* pp. 76 and 114), but is supposed to be present in aqueous solution. There is another circumstance remarkable with this acid. The carbonyl (CO, fig. 527, p. 130) is patronising both hydroxyls, so that there are, in a sort of way, two carboxyls, each of the hydroxyls having a half share in the carbonyl, and this constitutes the acid a di-basic acid; in point of fact, it is so, and this acid will therefore be mentioned amongst the di-basic acids (p. 184), although its correct place is here, when we look upon its structure as a combination of the group *carboxyl* with the *alcoholic hydroxyl* group, in which case the combination with the second base would not be a salt-formation proper, but an alcoholate. What we generally term carbonic acid is strictly carbon di-oxide (*vide* p. 184).

From *acetic acid* (fig. 667, p. 175) by introduction of, or from *glycol* (fig. 364, p. 76) by oxidation of, a hydroxyl, glycollic acid is derived:

Fig. 691

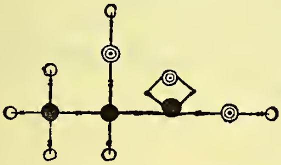


Glycollic acid, $C_2H_4O_3$; m.p. 80°; occurs in unripe grapes

Next derivative is from *propionic acid* (fig. 669, p. 176).

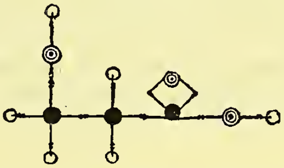
There is the choice of two places for the hydroxyl, consequently there are two acids

Fig. 692



*a*-Hydroxy-propionic acid, inactive ethidene- (ethylidene-) lactic acid, nanceïc-, thebolactic acid, lactic acid, $C_3H_6O_3$; syrupy liquid; forms anhydride when heated; occurs in sour milk, in the gastric juice in dyspepsia; used in diabetes, diphtheria, dyspepsia, diarrhœa, &c.

Fig. 693



*β*-Hydroxy-propionic acid, ethylene-lactic acid, hydracrylic acid, $C_3H_6O_3$; syrupy liquid; breaks up when heated

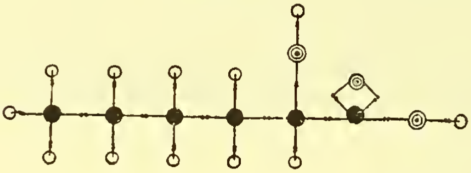
Though according to our theory only two lactic acids are possible, as a matter of fact there are four. Three of them, including the above-mentioned *a*-hydroxy-propionic acid or inactive lactic acid, are chemically almost identical, but differ in optical behaviour. Inactive lactic acid, as its name implies, has no influence on the polarised light; but there is one that turns the plane of light to the right termed active ethylidene lactic acid, *para-lactic*, or (because it is prepared from the juice of meat) *sarco-lactic acid*; and a third one (recently prepared from sugar by a bacillus) that turns the polarised light to the left, and therefore has the name of lævo-lactic acid (*Monatsh.* xi. p. 545).

The inactive acid is a combination of the two active compounds, neutralising each other's influence upon polarised light. There are, however, two ways in which this may be effected: either by the opposing activity of an equal number of molecules of the two acids, as in the inactive lactic acid, or in certain cases, to be subsequently mentioned, by the molecules exchanging halves of their chain (compare tartaric acid, p. 188).

To make the cause of such physical differences intelligible by geometrical drawings (compare p. 50) would in some cases require another system of figures by which the facilities of perspicuity and comparability would be lost. I prefer therefore to reserve the explanation of these differences to the stereo-chemical theories, pp. 461 &c.

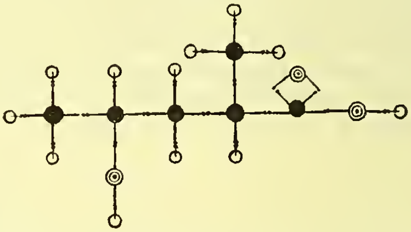
There are four hydroxy-butyric acids, six hydroxy-valeric acids, and twelve hydroxy-caproïc acids actually known. Of these it is unnecessary to specify but two, viz. leucic acid and *α*-methyl-*γ*-hydroxy-valeric acid, both hydroxylated caproïc acids:

FIG. 694



Leucic acid, α-hydroxy-caproïc acid, $C_6H_{12}O_3$; m.p. 73°

FIG. 695



α-Methyl-γ-hydroxy-valeric acid, $C_6H_{12}O_3$; unstable

Of the still higher homologues hydroxy-margaric and hydroxy-stearic acids may be mentioned.

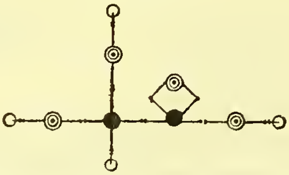
Two isomers of the former are said (*Journ. pr. Ch.* xxxvii. p. 53) to have been prepared, the hydroxyl in one of them being in *α*-, in the other in *γ*-position.

The latter forms a lactone (*vide* p. 182).

## Di-hydroxy-acids

As the first of these acids is derived from *acetic acid*, the two hydroxyls introduced must attach themselves to the same carbon-atom, there being no alternative:

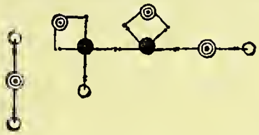
FIG. 696



Glyoxalic acid, glyoxylic acid, $C_2H_4O_4$; crystals; occurs in unripe fruit

On account of the hydroxyls' proximate position, water is frequently eliminated with the formation of an acid of such structure:

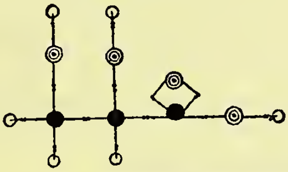
Fig. 697



This is an acid in which there is an aldehyde group (*vide* figs. 530 and 531, p. 130), and therefore, properly, belonging to aldehyde acids, a class to be subsequently mentioned (p. 227). The acid assumes, probably, now one form, now another, according to circumstances.

Another of the series is glyceric acid:

Fig. 698



Glyceric acid, $C_3H_6O_4$; syrupy fluid; changes into anhydride by heat

An isomeric acid in which the two hydroxyls are joined to the same (*a*-) carbon-atom is known, but only as chlorine-derivative. The acid itself cannot be isolated for reasons several times mentioned (see above).

Of higher homologues there are di-hydroxy-stearic acid, $C_{18}H_{36}O_4$, m.p. 136°·5. and di-hydroxy-jecoleïc acid, $C_{19}H_{38}O_4$, m.p. 114–116°, the di-hydroxy acid of the recently discovered *jecoleïc acid* in cod-liver oil.

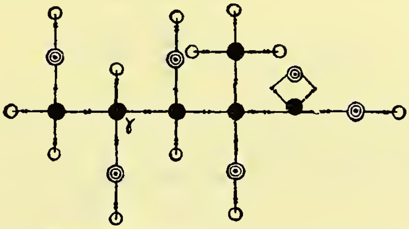
## Tri-hydroxy-acids

Besides the normal erythro-glucinic or erythritic acid, $C_4H_8O_5$, tri-hydroxy-stearic acid, $C_{18}H_{36}O_5$, m.p. 140°, and its stereo-isomer, iso-tri-hydroxy-stearic acid, m.p. 110°, derived from *ricinoleïc acid*, and two others from *ricin-elaïdic acid* (*vide* p. 195) must be mentioned.

## Tetra-hydroxy-acids

Three isomers are derived from hydroxy-caproïc acids. One of them, from *a*-methyl *γ*-hydroxy-valeric acid (fig. 695, p. 180), is saccharinic acid (*not to be confounded with the di-basic saccharic acid*, fig. 732, p. 188):

Fig. 699



(Gluco-) saccharinic acid, $C_6H_{12}O_6$ (*Beilst.* i. p. 667)

When heated, a molecule of water is eliminated, formed from the carboxyl's hydroxyl and the hydroxyl's hydrogen-atom of the γ-link; and the chain bending forms a ring in order to unite the two valencies disengaged by the departure of the hydroxyl and the hydrogen-atom.

Fig. 700

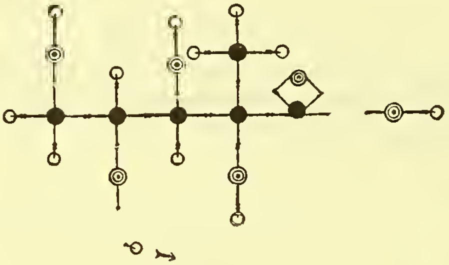
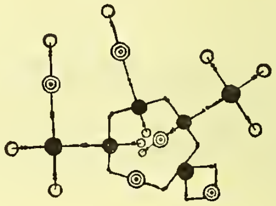


Fig. 701



Saccharin, $C_6H_{10}O_5$; m.p. 160°; bitter taste

Must not be confounded with the fashionable saccharine (*vide* fig. 1308, p. 368), which is so exceedingly sweet.

The isomeric acids form corresponding saccharins.

Many of the hydroxy-acids, particularly those with their hydroxyl in γ-position, like the above, have a great tendency to form a similar ring at that end of the chain. The product of this intramolecular ring-formation in an acid is termed a lactone or an intra-molecular anhydride.

Some α- and supposed β-lactones are also known, but as a rule the hydroxyl in β-hydroxy-acids does not take the hydrogen-atom from carboxyl, but from the link at the other side of it, creating a double bond between the two links:

Fig. 702

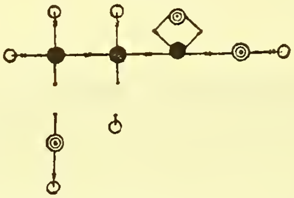


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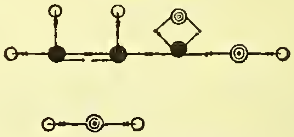
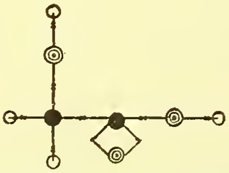
Fig. 703



β-Hydroxy-propionic acid − water = Acrylic acid + water

Authorities do not agree upon the behaviour of α-hydroxy-acids. One opinion is that they form a lactone analogous to the *glycides* (*vide* p. 116)

Fig. 704



Glycollic acid (fig. 691, p. 179)

Fig. 705

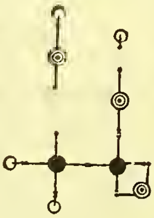
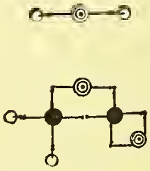
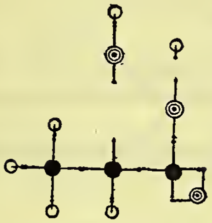


Fig. 706



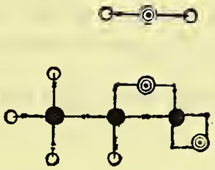
Glycolide, $C_2H_2O_2$; m.p. 220°

FIG. 707



Ethylidene-lactic acid

FIG. 708



Lactide, $C_3H_4O_2$; m.p. 125°

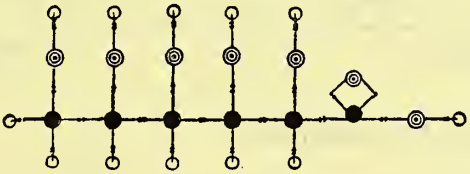
It is, however, more probable that neither glycolide nor lactide are the products of intramolecular anhydration, but that each of them is composed of two or more molecules of the acids, and therefore are regular anhydrides. As such they will be subsequently mentioned (*vide* p. 257). As regards glycolide see *Ber.* xxv. p. 3511, and xxvi. p. 262.

After this little deviation from our straight path we can finish our discussion of the tetra-hydroxy-acids by mentioning normal tetra-hydroxy-stearic acid or sativic acid, $C_{18}H_{36}O_6$, m.p. 173°. Sativic acid may be converted into stearic acid; its structure is therefore normal, but there is no evidence conclusively showing the exact positions of the hydroxyls.

## Penta-hydroxy-acids

We know several isomeric compounds of six carbon-atoms belonging to this series: gluconic, para-gluconic, lactonic or galactonic, mannonic, glucogenic (?) acids. Most of them have a normal structure:

FIG. 709



Those which are derived from sugars by oxidation (gluconic, galactonic, mannonic acids) are re-converted into the original sugar by reduction of their lactones (*Ber.* xxii. p. 2204, and xxiii. p. 930).

The isomeric differences are most probably the various arrangements of the hydroxyls, some standing upright, others hanging down as demonstrated of the grape-sugar group (p. 153), these acids being obtained from the sugars. We cannot tell yet, with any degree of certainty, whether the hydroxyls point upwards or downwards; therefore they are in this treatise handled arbitrarily as the convenience of illustrating the progress of a process may require.

## Hexa-hydroxy-acids

Besides the little known triglycollic ($C_6H_{12}O_8$) and carbo-gluconic ($C_7H_{14}O_8$) acids (the first of which may perhaps belong to quite a different series of acids, and the second is only probably one of this series), we have hexa-hydroxy-stearic acids termed linusic acid, $C_{18}H_{36}O_8$, m.p. 204°, and iso-linusic acid, $C_{18}H_{36}O_8$, m.p. 174° (*Monatsh.* viii. p. 159 and ix. p. 180), obtained from *linolenic* and *iso-linolenic acids* (p. 198).

By the structure of these acids the structure of the hexa-hydroxy-acids is determined.

### Octa-hydroxy-acids

The only known member of this series is octa-hydroxy-margaric acid. It is derived from *therapic acid* (*vide* p. 198), and causes the well-known eructations after taking cod-liver oil. It has not been isolated.

No acids with more than eight hydroxyls are known, and we will therefore pass on to describe the

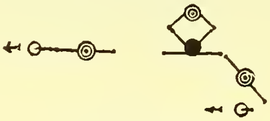
## Di-basic Acids

of the saturated series. They are characterised by the presence of two carboxyls in the chain.

### HYDROXYL-FREE ACIDS

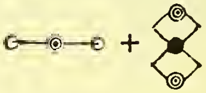
The first acid is formed from *formic acid* (fig. 666, p. 175), and is already referred to (p. 179) under the mono-basic mono-hydroxy-acids, viz. carbonic acid. From reasons there stated it is referred to this series, both its hydrogen-atoms being easily replaceable by basic bodies. It is not known in the free state, decomposing into water and carbon di-oxide (generally called carbonic acid)

Fig. 710



Carbonic acid

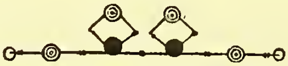
Fig. 711



Water + Carbon di-oxide

From *acetic acid* (fig. 667, p. 175) is derivable

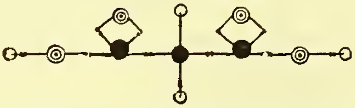
Fig. 712



Oxalic acid, $C_2H_2O_4$; m.p. 189°·5; crystals, subliming upon cautious, decomposing upon rapid heating; poisonous; occurs in many plants, *oxalis*, *rumex*, *rhubarb*, &c., mostly as salts; some urinary calculi consist of the calcium or ammonium salt; human urine contains, probably always, minute quantities, in some diseases more. Commercial salt of sorrel is a potassium oxalate (in which potassium has replaced one of the hydrogen atoms) in combination with another molecule of oxalic acid

From *propionic acid* (fig. 669, p. 176) is derivable

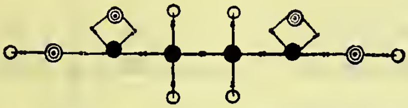
Fig. 713



Malonic acid, $C_3H_4O_4$; crystals; m.p. 134°; occurs in beet-root

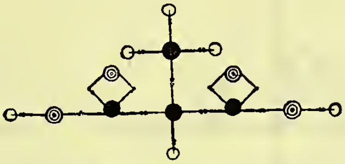
From the *butyric acids* (figs. 670 and 671, p. 176) two corresponding di-basic acids are derived:

Fig. 714



Common succinic- or ethylene-succinic acid, symmetrical ethane-di-carboxylic acid, $C_4H_6O_4$; m.p. 185°

Fig. 715

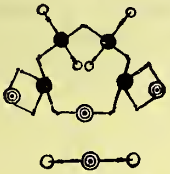


Iso-succinic- or ethylidene-succinic acid, $C_4H_6O_4$; m.p. 130°

The two acids behave differently when heated. The first forms a lactone, the other breaks up into propionic acid and carbon di-oxide (carbonic acid). The processes will be understood without further display if we refer to the formation of lactones (p. 182).

From succinic acid:

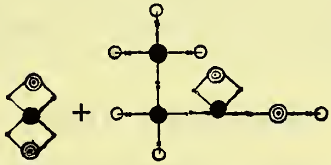
Fig. 716



Succinic anhydride (lactone) m.p. 120°

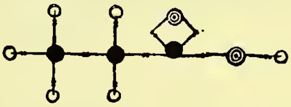
From iso-succinic acid:

Fig. 717



Carbon di-oxide +

Fig. 718

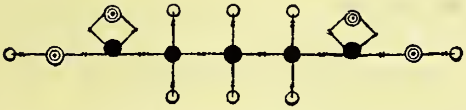


or

Propionic acid

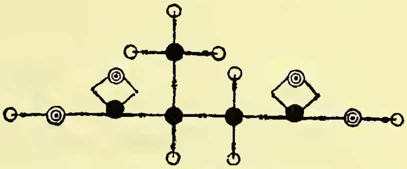
From each of the four *valeric acids* a di-basic acid may be derived and has been prepared. Two of these are

Fig. 719



Glutaric acid, normal pyrotartaric acid, $C_5H_8O_4$; m.p. 97°·5

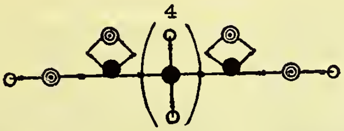
Fig. 720



Pyrotartaric acid, methyl-succinic acid, $C_5H_8O_4$; m.p. 112°

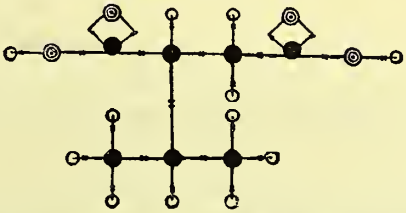
Amongst the higher homologues derivable from *caproïc*, *œnanthylic*, *caprylic*, *pelargonic*, and *capric acids*, or their isomers, the undermentioned have more or less interest.

Fig. 721



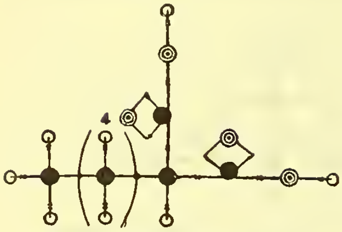
Adipic acid, $C_6H_{10}O_4$; m.p. 149°; eight isomeric acids besides are known

Fig. 722



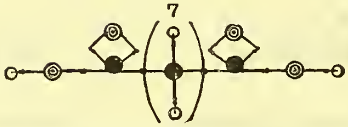
Pimelic acid, $C_7H_{12}O_4$; m.p. 103°; nine other isomers are known, including the normal

Fig. 723



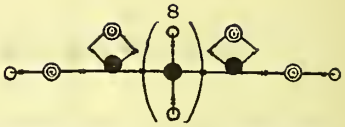
Pentyl-malonic acid, $C_8H_{14}O_4$; m.p. 82°; amongst its five isomers is suberic acid (m.p. 141°), probably the normal acid

Fig. 724



Normal azelaïc acid, $C_9H_{16}O_4$; m.p. 107°; azelaïc or lepargylic acid (m.p. 106°) is the only isomer known, but its structure has not been ascertained

Fig. 725



Sebacic acid, $C_{10}H_{18}O_4$; m.p. 133° (comp. p. 194)

As regards melting-point these acids show the same behaviour as the fundamental acids (*vide* p. 178), with the remarkable exception that even numbers form a descending scale, whereas odd numbers, with the exception of the first, form an ascending scale:

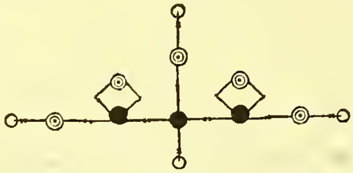
| Number of carbon-atoms . . | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|
| Melting-point of even numbers . | 189°·5 | | 185° | | 149° | | 141° | | 133° |
| Melting point of odd numbers . | | 134° | | 97°·5 | | 103° | | 107° | |

# HYDROXY-ACIDS

## Mono-hydroxy-acids

By introducing a hydroxyl into *malonic acid* (fig. 713, p. 184), we have

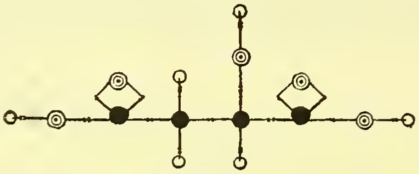
Fig. 726



Tartronic acid, hydroxy-malonic acid, $C_3H_4O_5$; m.p. 186°, breaking up at that temperature

By the same process *succinic acid* (fig. 714, p. 185) becomes

Fig. 727

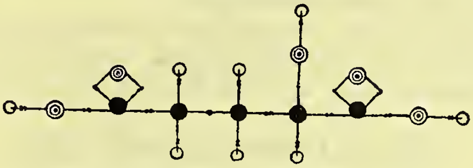


Malic or hydroxy-succinic acid, $C_4H_6O_5$; m.p. 100°; occurs widely distributed in the vegetable world; recommended as an effective expectorant

Besides an isomer formed from *iso-succinic acid* (fig. 715, p. 185), m.p. 178° (decomp.), there are three optically different malic acids, all having the same linking structure. Their structural differences will be explained by the stereo-chemical theory (*vide* pp. 461 &c.).

From *glutaric acid* (fig. 719, p. 185):

FIG. 728



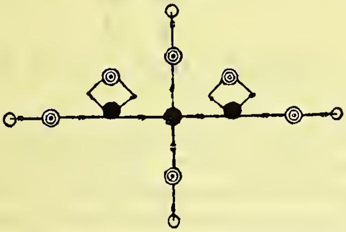
α-Hydroxy-glutaric acid, $C_5H_8O_5$; m.p. 72°

Amongst its eight isomers are *hydroxy-pyro-tartaric*, *itamalic*, and *citramalic acids*; they are all structural isomers, besides which there are stereo-isomers.

## Di-hydroxy-acids

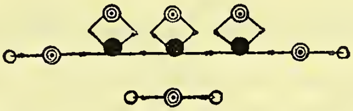
When we add another hydroxyl to tartronic acid (fig. 726, p. 186) we have no other carbon-atom to attach it to than the one already charged with a hydroxyl; this is, as we know, an awkward position for a carbon-atom—a situation it tries to get out of as soon as there is an opportunity by discharging one of the hydroxyls in form of water. The acid thus produced, mesoxalic acid, has therefore probably two forms of which it makes use, as circumstances necessitate, in analogy to glyoxalic acid mentioned on p. 180.

FIG. 729



or

FIG. 730

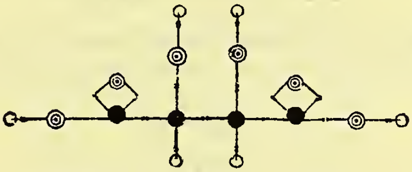


Mesoxalic acid, $C_3H_4O_6$ or $C_3H_2O_5$; m.p. 115°

The second structure belongs to ketone acids (*vide* p. 227).

By introducing two hydroxyls into *succinic acid* (fig. 714, p. 185), or a second one into *malic acid* (fig. 727, p. 186), we get tartaric acid.

FIG. 731



Tartaric acid, $C_4H_6O_6$; m.p. 170°

There are four acids of the above structure, almost identical in their chemical properties, but there are optical differences in three of them, and between the two optically alike there are some minor chemical differences: one is dextro-, another lævo-rotatory, and the other two are inactive. The first is termed dextro-tartaric acid, the second lævo-tartaric acid, and the others racemic acid and meso-tartaric acid respectively.

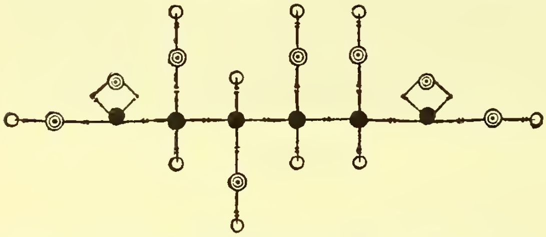
The difference between dextro- and lævo-tartaric acids is easily explicable by the stereo-chemical theory, as in similar cases mentioned before (*vide* malic acid, p. 186), and will be subsequently more fully discussed. In racemic acid there are equal numbers of molecules of each of these two acids present, and every molecule in meso-tartaric acid is composed of half a molecule dextro- and half a molecule lævo-tartaric acid.

In our figures these isomerisms may be expressed by making one of the hydroxyls hang down in dextro-tartaric acid; reverse the positions of both hydroxyls in the lævo-compound, and meso-tartaric acid would be represented by the preceding fig. 731 (*vide* figs. 1579 to 1581, p. 464).

### Tri- and tetra-hydroxy-acids

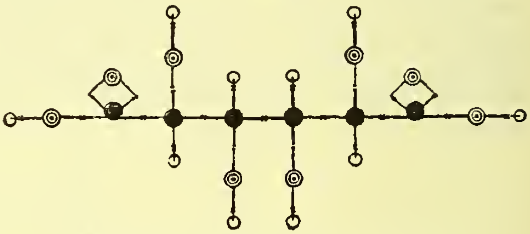
There are no tri-hydroxy-acids of sufficient interest; but of tetra-hydroxy-acids, saccharic and mucic acids attract our attention. They are normal acids, and their only difference of structure consists in the positions of the hydroxyls, as explained under the grape sugar group, p. 153, and the mono-basic-penta-hydroxy-acids, p. 183, and the tartaric acids above. Accordingly two of the acids may be represented thus (*Ber.* xxiv. p. 2685):

Fig. 732



Saccharic acid, $C_6H_{10}O_8$; m.p. 130–132°
(saccharinic acid is a different compound, *vide* fig. 699, p. 181)

Fig. 733



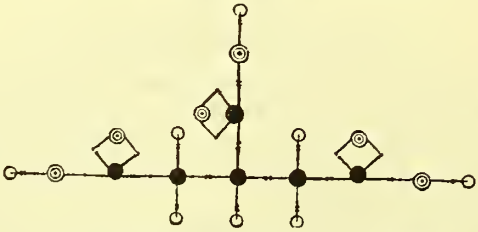
Mucic acid, $C_6H_{10}O_8$; m.p. 213° decomp.

Mucic acid is optically inactive; but there are two optically different, besides an inactive, saccharic acids; one of the active acids may be represented as above, the other by reversing the positions of all the hydroxyls; the inactive acid is a mixture of an equal number of molecules of each of the two others, and mucic acid is composed of half a molecule each of the two active forms, all bearing the same relation to each other as the tartaric acids; another series of isomeric acids, $C_6H_{10}O_8$, mutually related in exactly the same way, are the three manno-saccharic-acids and allo-mucic acid, the latter corresponding to mucic and meso-tartaric acids (for stereo-chemical explanation *vide* p. 464).

## Tri-basic Acids

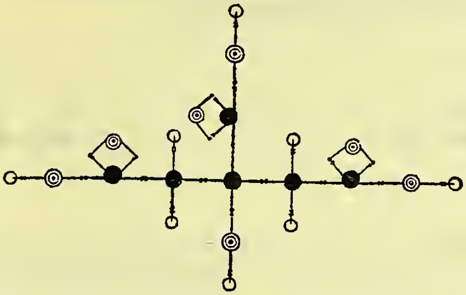
There are but few tri-basic acids known, and of them only three to be mentioned here, one *hydroxyl-free*: tri-carballylic acid; one *mono-hydroxy-acid*: citric acid; and one *di-hydroxy*: desoxalic acid.

Fig. 734



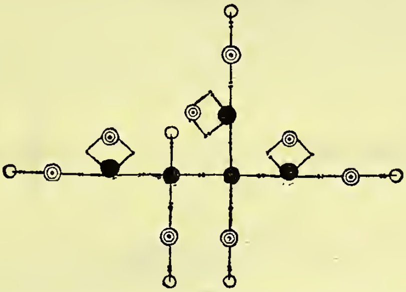
Tri-carballylic acid, $C_6H_8O_6$; m.p. 166°

Fig. 735



Citric acid, $C_6H_8O_7$; m.p. 153°; occurs in lemon and other sour fruits, in tobacco, in milk, in the sap of the vine (only in the spring); can be synthetically prepared from *glycerin*

Fig. 736



Desoxalic acid, $C_5H_6O_8$; easily decomposed on heating

## Tetra-, Penta-, and Hexa-basic Acids

None of them occur in nature. The examples set out in Table II., p. 173, are sufficient for our purpose.

# UNSATURATED ALIPHATIC ACID SERIES

## *ETHYLENE ACIDS*

## MONO-ETHYLENE ACIDS

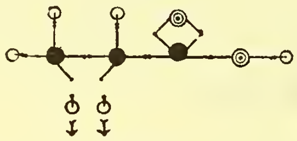
## Mono-basic Acids

### HYDROXYL-FREE. OLEÏC SERIES

These acids may be considered derived from the fundamental saturated acids by the removal of two hydrogen-atoms, and may be reconverted to them by restoring the two hydrogen-atoms removed.

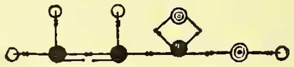
In them two carbon-atoms are joined by a double bond; consequently a third atom is required in order to form the carboxyl, and the simplest compound in the series must therefore consist of three carbon-atoms, and may be considered as derived from *propionic acid* (see Table I*a*, p. 171, and fig. 669, p. 176) by the removal of two hydrogen-atoms.

Fig. 737



Propionic acid

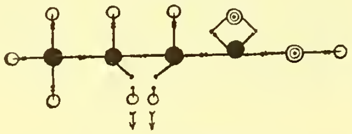
Fig. 738



Acrylic acid, $C_3H_4O_2$; b.p. 140°; very similar to propionic acid, to which it may be converted by reinstating the two hydrogen atoms removed

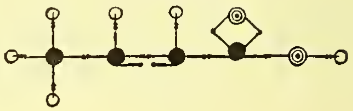
From *butyric acids* (figs. 670 and 671, p. 176) it is possible to derive three acids of this series, two from the normal acid by removing different pairs of hydrogen and one from the iso-acid; in addition an acid is known, which has the same geometrical structure as one of the derivatives from the normal compound, but differs in stereometrical respect.

Fig. 739



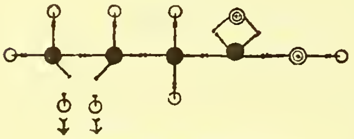
Normal butyric acid

Fig. 740



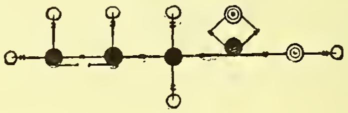
1. α-Crotonic acid, $C_4H_6O_2$; m.p. 72°
2. Stereo-isomer: iso-crotonic acid, liquid- (or erroneously β-) crotonic acid; b.p. 172°; changes on heating into crotonic acid

Fig. 741



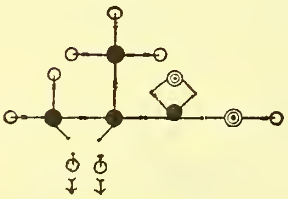
Normal butyric acid

Fig. 742



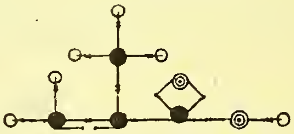
Vinyl-acetic acid, the true β-crotonic acid, $C_4H_6O_2$ (*Ber.* xvi. p. 2592; *Ann.* cclxvi. p. 358). This was formerly believed to be the constitution of iso-crotonic acid, hence its designation as β-crotonic acid

Fig. 743



Iso-butyric acid

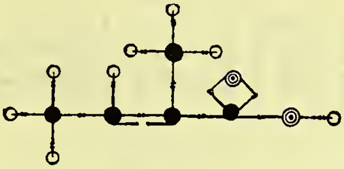
Fig. 744



Methacrylic acid, $C_4H_6O_2$; m.p. 16°, b.p. 160°; occurs in the oil of chamomile

From one of the isomers of *normal valeric acid* (methyl-ethyl-acetic acid) occurring in the fruits of *angelica archangelica*, two acids originate, which stand in the same relation to each other as crotonic- and iso-crotonic acid, viz. angelic acid and tiglic acid; their joint structure is represented by

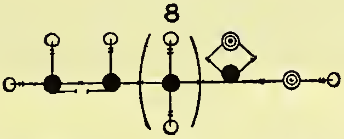
Fig. 745



1. Angelic acid, $C_5H_8O_2$; m.p. 45°; is found in the angelica root and in Roman chamomile oil
2. Tiglic acid, $C_5H_8O_2$; m.p. 64°; occurs in croton oil as glyceride, and in Roman chamomile oil

Only few of the higher homologues need mentioning, their exact constitution not being known with certainty. All the acids contained in natural fats have a straight chain as far as has been ascertained, but the difficulty is to locate the double bond. When we break up a doubly-linked chain we generally suppose, as stated before, that it parts at the double bond; therefore when we ascertain what the fragments are, the position of the double bond is a matter of course; still there are undoubted exceptions. The first higher homologue we have to mention is

Fig. 746

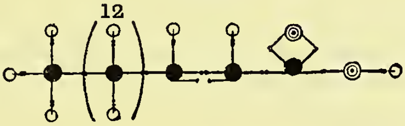


Undecylenic acid, $C_{11}H_{20}O_2$; m.p. 24°·5

Judging from its derivation from *ricinoleïc acid* (*vide* fig. 760, p. 194), the structure, which is a strictly normal one (comp. p. 20), should be correct.

Of homologues with the following structure

Fig. 747

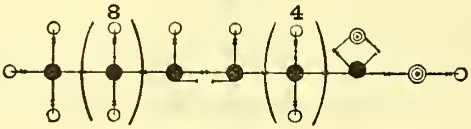


there are three acids, of which two are stereo-isomeric; the isomeric difference of the third is not known:

1. Hypogæïc acid, $C_{16}H_{30}O_2$, m.p. 33°, occurs in earth-nut oil. When distilled yields sebacic acid (fig. 725, p. 186).
2. Gæïdinic acid, $C_{16}H_{30}O_2$, m.p. 39°, is a stereo-isomer of hypogæïc acid, and stands to that acid in the same relation as crotonic to iso-crotonic, angelic to tiglic acid.
3. Physetoleïc acid, $C_{16}H_{30}O_2$, m.p. 30°, is found in spermaceti oil from the sperm-whale. Does not yield sebacic acid.

Assuming the rule to be correct that compounds with double bonds break up into smaller pieces at the place or places where there are such bonds, hypogæïc acid, yielding sebacic acid ($C_{10}H_{18}O_4$) should, as regards the double bond, have such structure:

Fig. 748

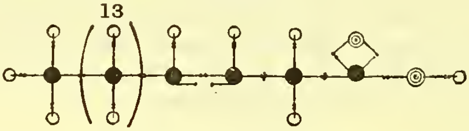


Hypogæïc acid

Doubly linked acids with seventeen carbon-atoms are unknown, but with eighteen we know of oleïc acid and its isomers, elaïdic acid and iso-oleïc acid.

Oleïc acid and elaïdic acid have one structure which has been differently interpreted as either one or other of these [1]

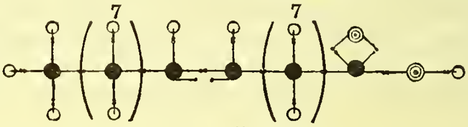
Fig. 749 A



*Journ. pr. Ch.* xxxvii. p. 6

or

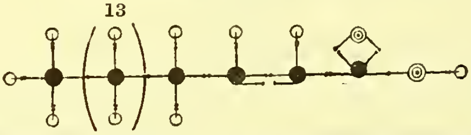
Fig. 749 B



*Ber.* xxvii. p. 173

1. Oleïc acid, $C_{18}H_{34}O_2$, solidifies at 4°, melts again at 14°. Its behaviour towards phenyl-hydrazine confirms the supposition that the double bond is not close to the carboxyl (*Ber.* xxvi. p. 118). It is present, joined to glycerin, in nearly all fats or fatty oils, particularly in olive- and almond-oil. 2. Stereo-isomer: elaïdic acid, $C_{18}H_{34}O_2$, m.p. 45°, does not occur in nature, but is prepared from oleïc acid, like gæïdinic acid from hypogæïc acid, and is a stereo-isomer of oleïc acid analogous to the other stereo-isomeric acids mentioned.

Fig. 750

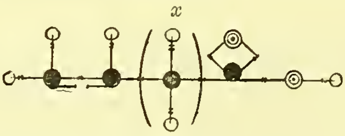


Iso-oleïc acid, $C_{18}H_{34}O_2$, m.p. 44°, has, according to the first of the above authorities, this structure, the double bond shifting from β- to α-position

There are two isomers with nineteen carbon-atoms, viz. dœglic acid and jecoleïc acid. We know scarcely anything of dœglic acid beyond that it is yellow, solidifies on cooling exactly like most other fatty oils. Jecoleïc acid is so recently discovered, as one of the essential constituents of cod-liver oil, that not much information is to be had about it; both because it easily breaks up and because its di-hydroxy-acid (*vide* p. 181) has a lower melting-point than its lower homologue di-hydroxy-stearic acid, it is most likely an iso-compound as regards its double bond. On account of its easy decomposition it has not yet been prepared in the free state. From this fact it may perhaps be concluded that dœglic acid and jecoleïc acid are isomeric, and not identical.

A normal acid of this division would have the following structure:

Fig. 751



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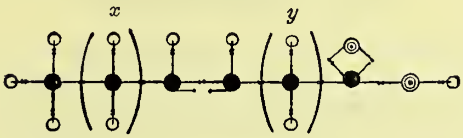
[1] The structures of stearolic acid, p. 199, and stearoxylic acid, p. 200, must be altered accordingly.

and an iso-acid would be

FIG. 752

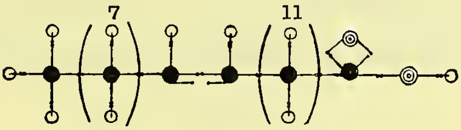


($x+y=15$) Jecoleïc acid, $C_{19}H_{36}O_2$

It is not likely that jecoleïc acid has side-chains, as no acid derived from natural fats has as yet been found to have any; they have all, without exception, straight chains, as already mentioned.

The last of these ethylene-acids has twenty-two carbon-atoms, and exists in two stereo-isomeric modifications: erucic and brassidic acids. They are so far interesting compounds as that the correctness of applying the stereo-chemical theory to these isomers has recently been conclusively proved by some elegant experimental researches (*Ber.* xxiv. p. 4120). Supposing the double bond to take up the position between the 13th and 14th carbon atom (*Ber.* xxvi. p. 1867), their structural formula may be rendered thus:

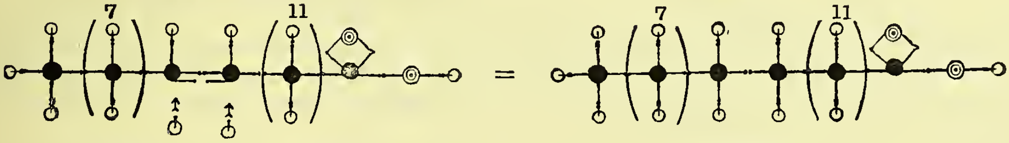
FIG. 753



1. Erucic acid, $C_{22}H_{42}O_2$; m.p. 34°; occurs in rape-seed oil and mustard oil
2. Brassidic or erucidic acid, $C_{22}H_{42}O_2$; m.p. 56°

All unsaturated ethylene-acids are converted into corresponding fundamental acids by addition of two hydrogen-atoms to the double bond, erucic-, to behenic acid, oleïc-, to stearic acid, angelic-, to valeric acid, &c.; *e.g.*

FIG. 754 FIG. 755



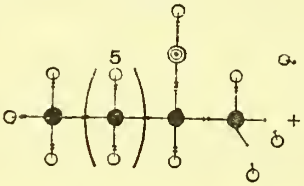
Erucic acid + two hydrogen atoms = Behenic acid

## HYDROXY-ACIDS

Only mono-hydroxy-acids of the mono-basic ethylene series are known; there are but few of them, and the only one of interest for our purpose is ricinoleïc acid, because it affords a good opportunity for demonstrating how conclusions are drawn as to the structure of doubly linked compounds, and how a clue to the structure of other compounds may be found at the same time.

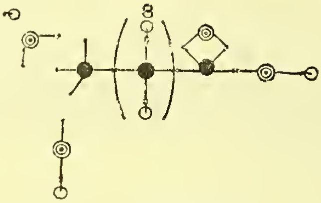
Ricinoleïc acid breaks up, on heating with alkalies, into two fragments: a secondary caproyl-alcohol (*methyl-hexyl-carbinol*) and *sebacic acid* (fig. 725, p. 186) (a hydrogen molecule being provided for by the alkali-hydrate):

Fig. 756



Secondary caproyl-alcohol

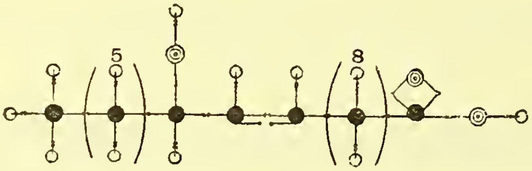
Fig. 757



Sebacic acid

That is strong evidence of this being the structure of ricinoleïc acid:

Fig. 758



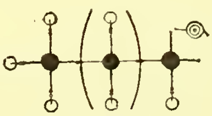
(*Ber.* xxi. p. 2734)

Ricinoleïc acid, $C_{18}H_{34}O_3$; oily liquid, decomposing on heating; occurs joined to glycerin in castor oil

Further, it has been experimentally proved that ricinoleïc acid is converted into stearic acid by *addition* of two hydrogen-atoms and by *substitution* of the hydroxyl by a third hydrogen-atom, and we know that stearic acid is a normal compound. From the first of these reactions, the *addition* of two hydrogen-atoms, we conclude the presence of a double bond, and from the formation of normal stearic acid we conclude that sebacic acid also must have a normal structure, and the secondary caproyl-alcohol a straight chain.

This structure of ricinoleïc acid is confirmed by distilling it under diminished pressure, when it breaks up into œnanthol (fig. 544, p. 132) and undecylenic acid (fig. 746, p. 191; *Ber.* x. p. 2035):

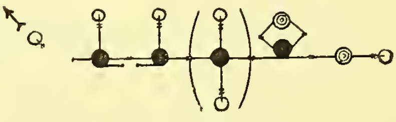
Fig. 759



Œnanthol

+

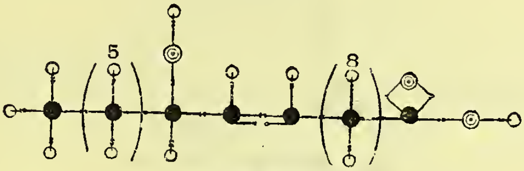
Fig. 760



Undecylenic acid

consequently the structure of ricinoleïc acid should be

Fig. 761



Ricinoleïc acid

If the conclusions are correct, it follows that œnanthol is a normal structure, and that undecylenic acid should have the structure given at p. 191. However, it is just possible, though not probable, that an intramolecular re-arrangement occurs analogous to what takes place in the acetylenes (*vide* p. 40).

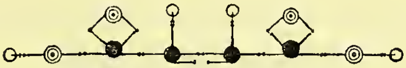
From ricinoleïc acid a stereo-isomeric acid, analogous to iso-crotonic, tiglic, gæïdinic, elaïdic, and brassidic acids, is derived. It is termed ricinelaïdic acid.

When hydroxyls act upon ricinoleïc acid two of them add themselves to the double bond, changing it into a single bond, and the acid becomes then a stearic acid with three hydroxyls. They can attach themselves in two stereo-different ways; therefore there are two different tri-hydroxy-stearic acids to be derived from ricinoleïc acid: this gave rise to a belief in the existence of two different ricinoleïc acids—ricinolic and ricinisolic acids (*Monatsh.* ix. 1888, p. 475). Stereo-chemical considerations, however, are quite capable of explaining the formation of two different hydroxy-acids from one and the same acid (*Monatsh.* xiii. 1892, p. 326). From ricinelaïdic acid also two hydroxy-acids are obtainable; consequently four tri-hydroxy-stearic acids exist (*vide* p. 181).

## Di-basic Acids

are characterised by two carboxyls and a double bond. The lowest number of carbon-atoms forming one of these acids must be four; consequently it is to *butane*, *butyl alcohol*, or *butyric acid* we shall look for the formation of the first of them, of which there are two stereo-isomers:

Fig. 762

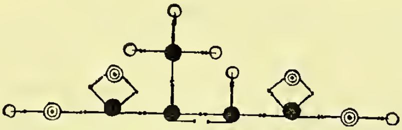


1. Fumaric acid, $C_4H_4O_4$ ; sublimes at 200° without melting, at the same time being converted partly into
2. Maleïc acid, $C_4H_4O_4$ ; m.p. 130°, which can again be converted into fumaric acid

Fumaric acid occurs in *Lichen islandicus*, *Fumaria officinalis*, and several other plants and fungi; maleïc acid does not occur in nature. They are practically convertible into succinic, malic, tartaric, &c., acids by judiciously introducing hydrogen-atoms and hydroxyls, and into butyric acid by methyl-substitution of carboxyl, thus going through the whole column *d* on Table I., pp. 171*a*, 171*b*.

Amongst the eight isomers of the next acid, derivable from valeric acid, we again meet with two stereo-isomeric acids:

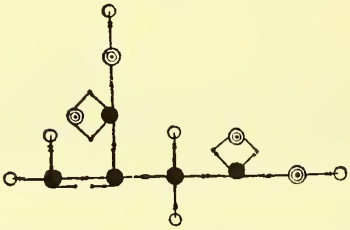
Fig. 763



1. Citraconic acid, $C_5H_6O_4$; m.p. 80°; and
2. Mesaconic acid, $C_5H_6O_4$; m.p. 202°

Another isomer is

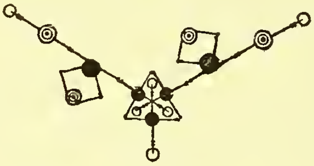
FIG. 764



Itaconic acid, $C_5H_6O_4$; m.p. 161°

The molecular refraction (*vide* p. 144) of the acid points to the absence of any double binding in it, and another structure has therefore been suggested (*Journ. pr. Ch.* ii. 31, p. 348; *Beilst*, i. p. 621), founded upon the tri-methylene structure (fig. 112, p. 24):

FIG. 765



Another structure of itaconic acid

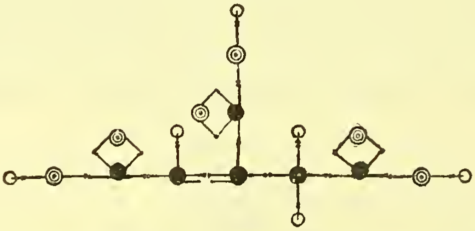
There is, however, an acid, tri-methylene di-carboxylic acid, of certainly this very structure but of properties widely different; therefore it is not probable that itaconic acid is thus correctly represented.

The other acids of this series do not require our attention, neither do the hydroxy-compounds.

## Tri-basic Acids

Only one is known with certainty, viz. aconitic acid:

FIG. 766



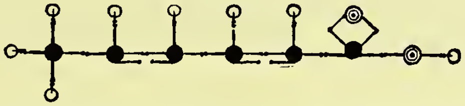
Aconitic acid, $C_6H_6O_6$; m.p. 186°; occurs in several *aconitum* species, sugar-cane, beet-root, &c.

Aceconitic, iso-aconitic, and pseudo-aconitic acids are believed to be isomers, but their structures have not been ascertained.

## DI-ETHYLENE ACIDS

But few di-ethylene-acids are known.
Sorbic acid is one of them, and its structure may be thus illustrated:

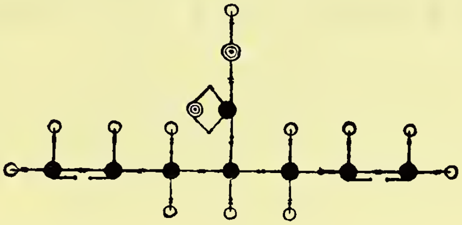
FIG. 766 A



Sorbic acid, $C_6H_8O_2$; m.p. 134°·5; occurs in unripe mountain-ash berries

Di-allyl-acetic acid is another with the following structure:

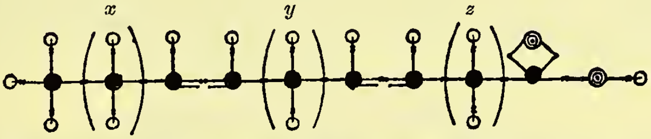
FIG. 766 B



Di-allyl-acetic acid, $C_8H_{12}O_2$; b.p. 222°; a laboratory product

Elæo-margaric acid has not been much examined as to its structure; it may, in a general way, be represented by

FIG. 767



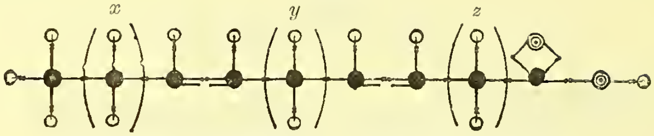
$x+y+z=11$. Elæo-margaric acid, $C_{17}H_{30}O_2$; m.p. 48°; occurs joined to glycerin in oil from the seeds of *Elæococca vernicia*

An isomer, elæolic acid, is also found in that oil, and another isomer, elæo-stearic acid (m.p. 71°), is formed from *elæo-margaric acid* on exposure to light. Some authorities suppose a triple bond in elæo-margaric acid, and call it margarolic acid.

Linoleïc acid used to be the name of the acid bound to glycerin in linseed oil, but recently it has been found to consist of several acids (*Monatsh.* viii. p. 147 *seq.*): linolic acid, $C_{18}H_{32}O_2$, linolenic acid, $C_{18}H_{30}O_2$, and its isomer, iso-linolenic acid.

The first of them belongs to this series:

FIG. 768



$x+y+z=12$; $y$ cannot be $=0$. Linolic acid, $C_{18}H_{32}O_2$

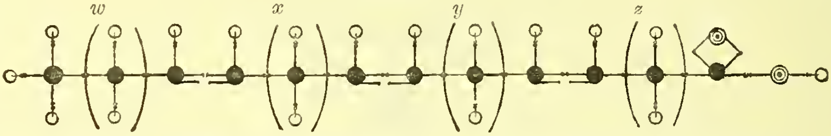
Some light has been thrown upon the constitution of this oil. We know there are no side-chains, because it may be converted into stearic acid (fig. 683, p. 178), and the double bonds are separated by at least one methylene (fig. 35, p. 11), and therefore $y$ cannot be $=0$.

On oxidation it yields sativic acid (p. 183).

## TRI-ETHYLENE ACIDS

The only ones known are linolenic acid and its isomer, iso-linolenic acid, expressed in a general formula thus:

FIG. 769



$w+x+y+z=10$; $w$ and $z$ may be $=0$, but $x$ and $y$ probably not. Linolenic acid, $C_{18}H_{30}O_2$

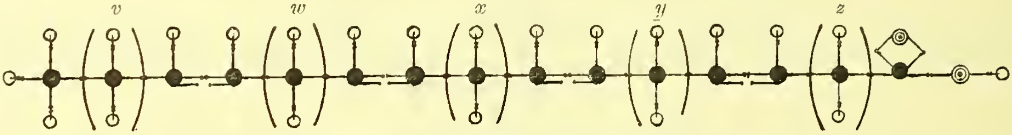
By oxidation it is converted into hexa-hydroxy-stearic (linusic) acid.

Nothing is known of the structure of iso-linolenic acid. It has not been isolated; it forms on oxidation an iso-hexa-hydroxy-stearic acid (iso-linusic acid).

## TETRA-ETHYLENE ACID

Therapic acid, just discovered in cod-liver oil by Heyerdahl, is the only known acid of this class. It has a straight chain and four double bindings, probably not close to the carboxyl; beyond this nothing is known of their position. It is only the bromine addition-product that it has been possible to prepare, the free acid being so susceptible of all reactions brought to bear upon it in order to isolate it that it at once splits up into a mixture of decomposition products. From its bromine-addition product we can conclude that the structure must be represented thus, when we remember that acids from natural fats have straight chains without any side-linkings:

FIG. 770



$v+w+x+y+z=7$. Therapic acid, $C_{17}H_{26}O_2$

As $v+w+x+y+z$ being $=7$, therapic acid has probably a structure in which $z=3$ and $v+w+x+y=4$, if not a strictly normal structure: $H_2C=(=C=)_3=CH-(CH_2)_{11}CO_2H$.

It is also remarkable as belonging, with its seventeen carbon-atoms, to the margaric acid family, which has so very few representatives (see Table I.) to boast of.

This is the last of the ethylene-acid series.

## *ACETYLENE ACIDS*

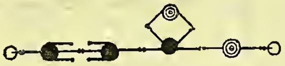
## MONO-ACETYLENE ACIDS

### Monobasic

These acids are characterised by a triple bond; the place in the chains, especially the longer ones, has been fully ascertained in a few instances only. In other cases I have uniformly placed it next to carboxyl, as it must be put somewhere.

The acids are not many, and only interesting from a theoretical point of view. The first is derivable from *propionic acid* (fig. 669, p. 176) by removal of four hydrogen-atoms:

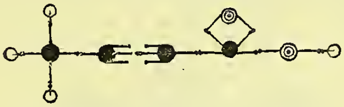
FIG. 771



Propiolic (propargylic) acid, $C_3H_2O_2$; b.p. 144°

From *butyric acid*:

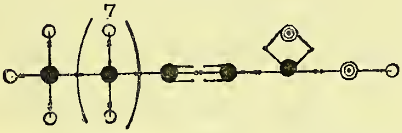
FIG. 772



Tetrolic acid, $C_4H_4O_2$; m.p. 76°·5

From *undecylic acid*:

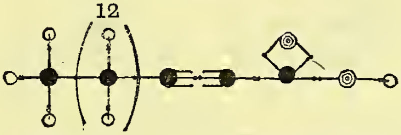
FIG. 774



Undecolic acid, $C_{11}H_{18}O_2$; m.p. 59°·5

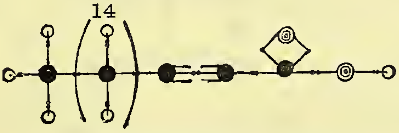
Amongst the higher homologues are

FIG. 775



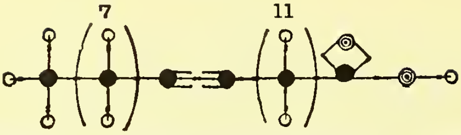
Palmitolic acid, $C_{16}H_{28}O_2$; m.p. 42°

FIG. 776



Stearolic acid, $C_{18}H_{32}O_2$; m.p. 48°

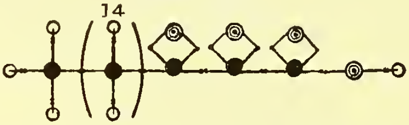
Fig. 777



Behenolic acid, $C_{22}H_{40}O_2$; m.p. 57°·5 (*Ber.* xxvi. p. 1867)

When acetylene acids are oxidised, hydroxy-acids are not formed because the hydroxyls would have to join the same carbon-atom, and, as we know, such compounds are very unstable, and can only exist under specially favourable circumstances; however oxy-acids (but not hydroxy-acids) are formed, each oxygen seizing both valencies of each carbon-atom. Therefore when, *e.g.* stearolic acid is oxidised, an acid is formed possessing this structure (*Annal.* cxl. p. 63):

Fig. 778



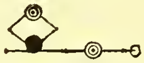
Stearoxylic acid, $C_{18}H_{32}O_4$; m.p. 86°

The structure of di-acetylene-mono-basic acids and of mono-, di-, and tetra-acetylene-di-basic acids are already given in Table IV. p. 174.

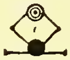
## ACID-RADICALS

Frequent use being made in the nomenclature, of radicals of acids, illustrated representations of those often met with may be acceptable: they are formed by removing hydroxyl from carboxyl, producing mono-valent radicals from mono-basic acids, and di-valent radicals from di-basic acids. In the case of hydroxy-acids, radicals are sometimes formed by removing alcohol-hydroxyls besides the hydroxyl in the carboxyl group, poly-valent radicals ensuing according to the number of hydroxyls removed. An enormous number of radicals may be formed conformably to these rules; therefore I can select but those most useful to know.

From fundamental acids by removing hydroxyl from carboxyl, mono-valent radicals are derived:

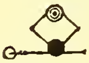


Carboxyl, $CO_2H$



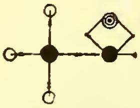
Carbonyl, CO

Fig. 779



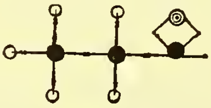
Formyl, CHO

Fig. 780



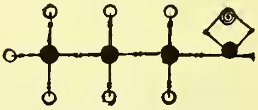
Acetyl, $C_2H_3O$

Fig. 781



Propionyl, $C_3H_5O$

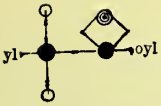
Fig. 782



Butyryl, $C_4H_7O$

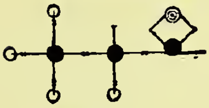
From hydroxy-acids of fundamental acids, di-valent radicals are formed by further removal of an alcohol hydroxyl:

FIG. 783



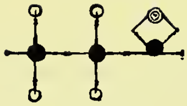
Glycollyl, $C_2H_2O$

FIG. 784



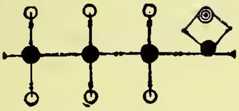
α-Lactyl, $C_3H_4O$

FIG. 785



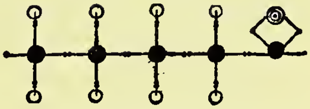
β-Lactyl, $C_3H_4O$

FIG. 786



Divalent γ-butyryl, $C_4H_6O$

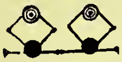
FIG. 787



Divalent δ-valeryl, $C_5H_8O$

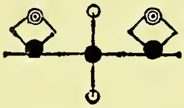
From di-basic acids, by removing the hydroxyls from both carboxyls, di-valent radicals:

FIG. 788



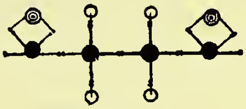
Oxalyl, $C_2O_2$

FIG. 789



Malonyl, $C_3H_2O_2$

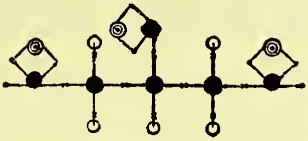
FIG. 790



Succinyl, $C_4H_4O_2$

and from three carboxyls, tri-valent radicals:

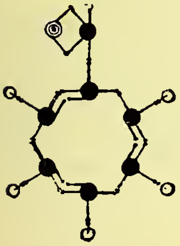
FIG. 791



Carballyl, $C_6H_5O_3$

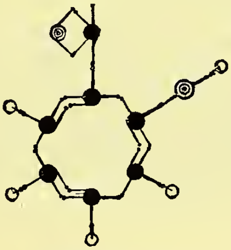
In order to have the acid radicals collected, some of the aromatic acids' radicals (*vide* p. 211) are given here by anticipation:

FIG. 792



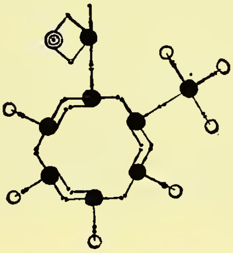
Benzoyl, $C_7H_5O$

FIG. 793



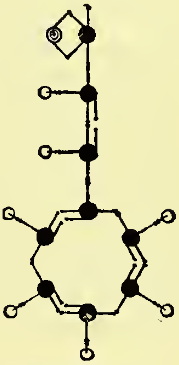
Salicyl, $C_7H_5O_2$

FIG. 794



o-Toluyl, $C_8H_7O$

FIG. 795



Cinnamyl, $C_9H_7O$

In exactly the same way other radicals of aromatic acids are formed and named.

## Future Nomenclature of Acids

According to the French proposal at the Congress, the names of acids are to be formed from the corresponding hydrocarbons by attaching, in the case of monobasic acids, the suffix *-oïque* to the name of the hydrocarbon; and in the case of di-, tri- (&c.), basic acids the suffix is to be *dioïque*, *trioïque*, &c.; 'corresponding hydrocarbon' is to be understood in the same sense as it has been used in this treatise, i.e. hydrocarbons with the same number of carbon-atoms, arranged in the same way as in the acid, and of which one or more have been converted into carboxyls.

The numbering of carbon-atoms in monobasic aliphatic acids without either side-chains, double or triple bonds, or substitutes commences with carboxyl's carbon; in all other cases the rules given for hydrocarbons are to be followed.

Formic acid (fig. 666, p. 175), for instance, being formed from methane, would in French receive the name of *acide méthanoïque*; in English, perhaps, *methanoïc acid*; acetic acid (fig. 667, p. 175), *ethanoïc acid*; oxalic acid (fig. 712, p. 184), *ethanedioïc acid*; succinic acid (fig. 714, p. 185), 1 : 4 *butanedioïc acid*; citric acid (fig. 735, p. 189) would probably be 3 *methyl* 3′ *pentanol* 1 : 3 : 5 *trioïc acid*; di-hydroxy-iso-citric acid (Table II. p. 173), 2 *methyl* 2′ : 3 : 4 *pentanetriol* 1 : 2 : 5 *trioïc acid*; buton-hexa-carboxylic acid (Table II. p. 173), 3 : 3′ : 4 : 4′ *methyl* 1 : 3 : 3′ : 4 : 4′ : 6 *hexanehexoïc acid.*

Lactones will have their names formed from the acids from which they are derived by transforming the suffix *-oïque* (*-oïc*) into *-olide*, the position of the alcoholic hydroxyl, through which the lactone formation has been effected, to be indicated by the ordinal number of the carbons as described under hydrocarbons, the addition of Greek letters in the usual way being optional. The only example given by the Congress is 'valerolactone,' formed from $\gamma$-hydroxy-valeric acid, and its name would consequently be 1 : 4 (or $\gamma$) *pentanolide.* A slightly more complicated lactone is saccharin (fig. 701, p. 182), which, I suppose, has to be termed 2 *methyl* 2′ : 3 : 5 *pentane-triol* 1 : 4 (or $\gamma$) *-olide.*

The names of mono-valent acid-radicals (*vide* p. 200) are to be derived from the corresponding acids by transforming the suffix *-oïque* into *-oyle.* Poly-valent radicals are not mentioned.

In a later, apparently authoritative, publication of the Congress Resolutions (*Agenda du Chimiste*, 1893, p. 468) containing sixty-two paragraphs, as against forty-six in earlier publications (vide *Nature*, May 19, 1892, p. 56), several important additions and modifications appear. Thus side-chains, in which a carboxyl is present, no longer derive their names from the corresponding hydrocarbons, but by adding the suffix *-oïc* to the name of the hydrocarbon radical; the group $CO_2H$, otherwise carboxyl, is in the quality of a side-chain termed *methyloïc*; $CH_2CO_2H$, *ethyloïc*, &c. This enables us to form a nomenclature for di-valent mono-basic acids' radicals also: glycollyl (fig. 783, p. 201) might be *ethyloyl*, $\alpha$-lactyl (fig. 784) = 2 *propyloyl*, $\beta$-lactyl = 3 *propyloyl*, &c., and mono-valent radicals, derived from di-basic acids by removing the hydroxyl from *one* of the carboxyls, might be distinguished by the suffix *-oyloïc*; e.g., the group $OC{-}CO_2H$ might be called ethanoyloïc (acid). From the important part radicals play in the principles of the nomenclature it is a pity that in so many instances we are left to guess at their names.

As a consequence of this change in the nomenclature of side-chains the systematic names of the above-mentioned acids will also have to be changed: citric acid would be 3 *methyloïc*-3 *pentanol-dioïc acid*, dihydroxy-iso-citric acid = 2 *methyloïc* 2 : 3 : 4 *pentanetriol dioïc* acid, buton-hexa-carboxylic acid = 3 : 3 : 4 : 4 *tetramethyloïc hexane-dioïc acid.* German chemists seem to prefer *diacid* (*disäure*) to *dioïc acid*, or *methyl-acid* (*methylsäure*) to *methyloïc acid.* In the above attempt at forming a nomenclature for poly-valent acid radicals the suffix *-oïc* or some other suffix cannot be dispensed with.

# Part VII.

# OXYGEN COMPOUNDS

## MUTUAL COMBINATIONS

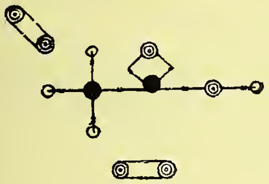
## OF

## HYDROCARBONS, ALCOHOLS, PHENOLS ALDEHYDES, ACIDS, ETC.

## CLASSIFICATION

The action of hydrogen-peroxide hitherto illustrated has been to build up from hydrocarbons, gradually, alcohols, aldehydes, or ketones, and acids. The further action of hydrogen-peroxide consists, not in building up any new compounds (excepting two unstable superoxides), but in pulling to pieces again what was built up: the ultimate products of oxidation of all organic compounds consisting of carbon, hydrogen, and oxygen, being water and carbon dioxide, or carbonic acid. The process being rather too complex with hydrogen-peroxide for illustrations, we will use oxygen molecules for our purpose.

Fig. 796



One molecule of acetic acid
two molecules of oxygen

Fig. 797

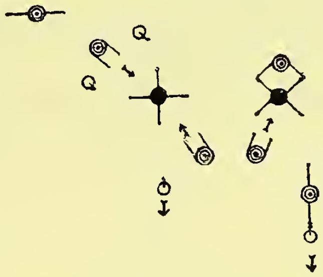
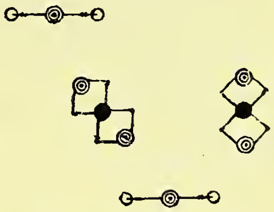


Fig. 798



Two molecules of carbon-dioxide
two molecules of water

Our resources of forming new compounds without invoking the assistance of other elements are, however, not exhausted; on the contrary, we have hitherto, as it were, only been preparing material for the real work to begin, and it is not solely the genius of man that performs the work, for even Nature herself takes a share in it, though, it must be admitted, only a comparatively small one. Human work is in this instance more thorough, though Nature is more skilful, and can produce things in comparison to which ours often are but clumsy imitations, and frequently not even that.

Our way of performing the work is very much in the cooking style: a little of this, a little of that, a sprinkling of seasoning, and *voilà* a new dish.

Thus we take the end of one thing and the beginning of another, sometimes two beginnings or two ends, or a middle part of a third is put between; here a little oxygen, carbonyl, or hydroxyl for seasoning, there a little hydrogen and such like for sweetening. Order must be kept in such a motley medley, and therefore we avail ourselves of our old expedient, classification.

An acid may be looked upon as consisting of two parts: carboxyl indicating the genus, and the rest indicating the species. To either of these or to both simultaneously members of all the classes of compounds discussed up to now, may be joined by separation of a molecule of water, if the union is effected through a hydroxyl; but otherwise by abstraction of our usual pair of hydrogen-atoms.

In this way new classes of bodies may be created dependent upon the sort of compounds joined, and upon where they are joined, i.e. whether the union takes place at the carboxyl end or at the opposite—we will call it *alkyl*—end of the acid, and also which end (in case of existing difference) the substituting body offers for the joining.

Accordingly the following new classes of compounds may be formed:

A. *Cyclo-acids*: By joining the alkyl-part of an acid to the hydroxyl-carbon of a phenol; or, in the case of a hydroxy-acid, by joining one of the hydroxyl-carbons to a cyclo-hydrocarbon.

B. *Aldehyde-acids*: By joining the carboxyl-part of formic acid (or the alkyl-part of an aldehyde) to the alkyl-part of an acid.

C. *Ketone-acids*: By joining the aldehyde-part of formic acid (or any other aldehyde-acid, or the alkyl-part of another acid) to the carboxyl-part of a second acid.

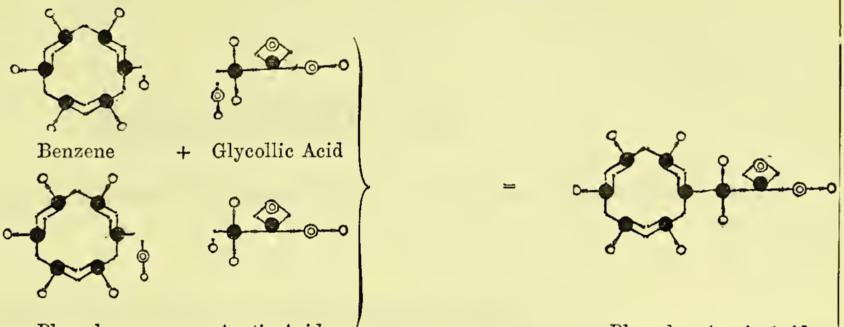
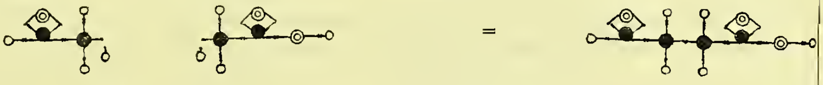
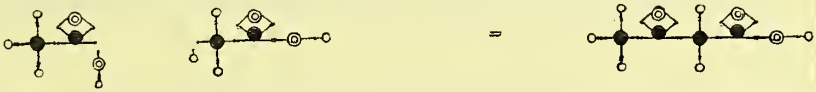
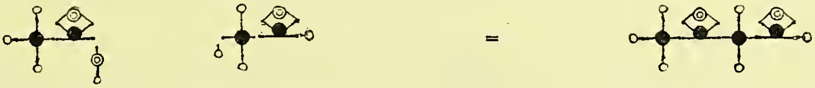
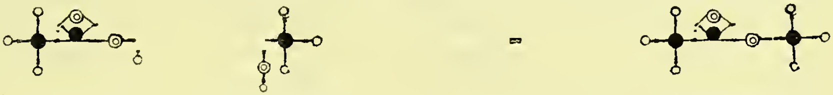
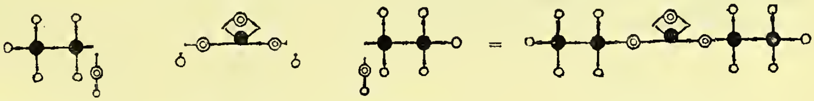
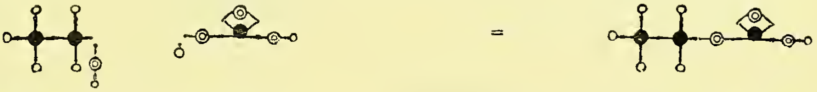
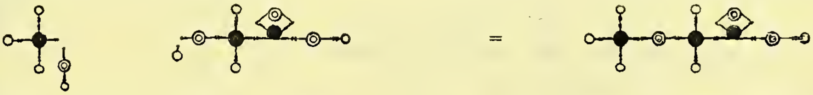
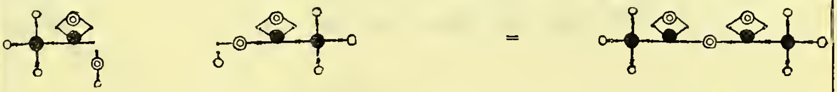
D. *Ketone-aldehydes*: By joining the carboxyl-part of an acid (aldehyde-acids excepted) to the alkyl-part of an aldehyde.

E. *Compound ethers*; 1, neutral: By joining the carboxyl-part of a monobasic acid (or all the carboxyl-parts of a polybasic acid) to an alcoholic or phenolic carbon of another compound;
2, acid: By joining one or more, but not all, carboxyl-parts of a polybasic acid to an alcoholic or phenolic carbon of another compound.

F. *Ether-acids*: By joining a hydroxy-acid and an alcohol or phenol through their alcoholic or phenolic carbons, and the carboxylic hydroxyl.

G. *Acid-anhydrides*: By joining the carboxyl-parts of two acids.

The formation of these compounds will be easily understood by the following illustrated schedule:

| | | |
|---|---|---|
| A | **Cyclo-acids**<br>*Hydrocarbon or Phenol and Acid*<br>*vide* p. 208 | <br>Benzene + Glycollic Acid<br>Phenol + Acetic Acid<br>= Phenyl – Acetic Acid |
| B | **Aldehyde-acids**<br>*Formic Acid or Aldehyde and Acid*<br>*vide* p. 227 | <br>Acetyl-aldehyde + Acetic Acid = Acetaldehyde – Acetic Acid (hypoth.) |
| C | **Ketone-acids**<br>*Acid and Acid*<br>*vide* p. 227 | <br>Acetic Acid + Acetic Acid = Aceto-acetic Acid |
| D | **Ketone-aldehydes**<br>*Acid and Aldehyde*<br>*vide* p. 230 | <br>Acetic Acid + Acetic Aldehyde = Aceto-acetic Aldehyde |
| E | **1. Neutral Compound Ethers**<br>*Acid and Alcohol or Phenol*<br>and | <br>Acetic Acid + Methyl-alcohol = Methyl-acetate<br><br>Ethyl-alcohol + Carbonic Acid + Ethyl-alcohol = Ethyl-carbonate |
| | **2. Acid Compound Ethers**<br>*Acid and Alcohol or Phenol*<br>*vide* p. 231 | <br>Ethyl-alcohol + Carbonic Acid = Ethyl-carbonic Acid |
| F | **Ether-acids**<br>*Hydroxy-acid and Alcohol or Phenol*<br>*vide* p. 250 | <br>Methyl-alcohol + Glycollic Acid = Methyl-glycollic Acid |
| G | **Acid-anhydrides**<br>*Acid and Acid*<br>*vide* p. 256 | <br>Acetic Acid + Acetic Acid = Acetic Anhydride |

# A. CYCLO-ACIDS

The first cyclo-hydrocarbon, it will be remembered, is *trimethylene* (fig. 112, p. 24), from which are formed

## 1. Trimethylene-carboxylic Acids

We have already mentioned that itaconic acid (p. 196), in the opinion of some chemists, is a trimethylene-derivative; that is, however, scarcely correct, because there is another legitimate possessor of that very structure, viz. trimethylene dicarboxylic acid, a compound quite distinct from itaconic acid (for illustration *vide* fig. 765, p. 196).

Several other acids of the same structure but with more or less carboxyls belong to this class.

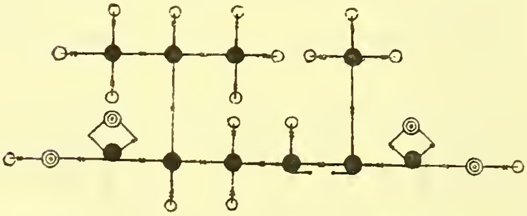
## 2. Tetramethylene-carboxylic Acids

formed by joining one or more molecules of carbonic acid to tetramethylene or its derivatives. They would not have required more than a passing attention had it not been for one or two chemists having propounded the tetramethylene form for an acid derived from camphor by oxidation, camphoric acid, which has harassed many chemical brains as much as her mother, camphor itself (*vide* p. 143 &c.). As discussions are still going on, an account of the several interpretations of its structure may be acceptable to those who wish to understand what they are all about, although only tetramethylene-structures strictly have their right place here. For better comparison I arrange those which have not hexagonal forms into that configuration also (compare diagonal-bond, p. 53), and place them in chronological order.

Proposed structures of camphoric acid, $C_{10}H_{16}O_4$, m.p. 180° (comp. also p. 144 &c.).

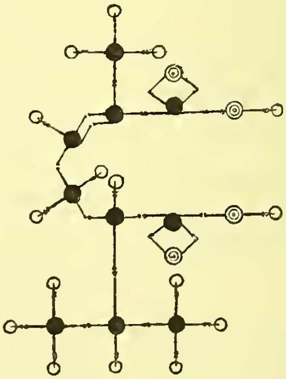
1873

Fig. 799



=

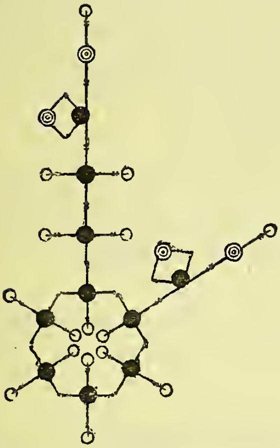
Fig. 800



Kekulé (*Ber.* vi. p. 932)

1873

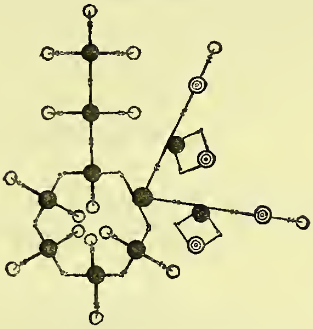
FIG. 801



Kachler (*Ann.* clxix. p. 192)

1877

FIG. 802



Wreden (*Ber.* x. p. 714)

1870 to 1892

FIG. 803

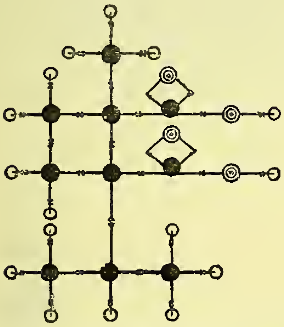


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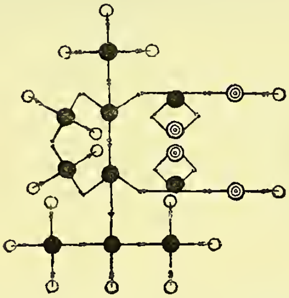
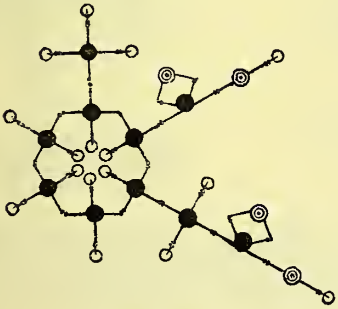
FIG. 804



Victor Meyer (*Ber.* iii. p. 121); Ballò (*Ber.* xiv. p. 337); Koenigs and Eppens (*Ber.* xxv. p. 267) &c.

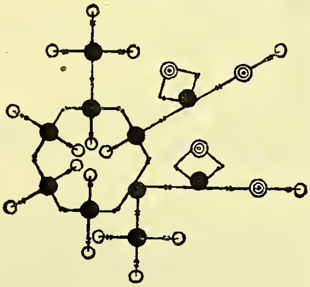
1892

FIG. 805



Marsh (*Proceed. Royal S.* xlvii. p. 6)

FIG. 806



Norman Collie (*Ber.* xxv. p. 1116)

In such an embarrassment of riches the difficulty of selection is increased when, on the one hand, authorities (*Jour. pr. Ch.* xlv. p. 475) tell us that the combustion-heat of camphoric acid agrees with its derivation from an aromatic chain, but not with any of the other structures; and when, on the other hand, it is asserted, by equally high authority (*Beilst*, i. p. 631), that the possibility of any structure with an aromatic chain is excluded because aromatic amido-acids are coloured red by furfurol and amido-camphoric acid is not affected.

Victor Meyer's &c. structure enjoys at present, I believe, most favour.

After this little détour we can again go on with our cyclo-acids.

## 3. Pentamethylene-carboxylic acids

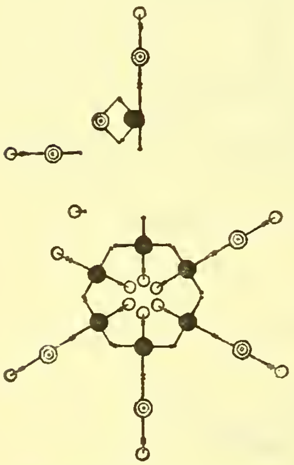
formed from one or more molecules of carbonic acid joining the cyclo-hydrocarbon have also been prepared, but need no further mention.

Amongst

## 4. Hexamethylene-carboxylic acids

there is one, quinic acid, that needs illustration: it may be considered a derivative of a hydrated (*vide* p. 33) *tetra-hydroxy-benzene*, similar to the one given in fig. 425, p. 94, but with the hydroxyls close together (2 : 3 : 4 : 5), and *carbonic acid*; or from a *penta-hydroxy-hexamethylene* (fig. 426, p. 94) and *formic acid*, in both cases a molecule of water being separated as explained by the formation of these acids in schedule p. 207.

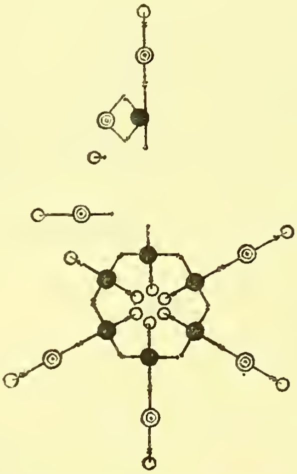
Fig. 807



Tetra-hydroxy-hexamethylene and carbonic acid

or

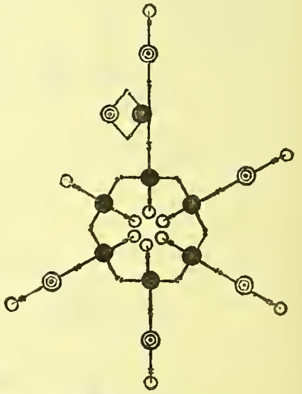
Fig. 808



Penta-hydroxy-hexamethylene and formic acid

=

Fig. 809



Quinic acid, hexahydro-tetra-hydroxy-benzoic acid, $C_7H_{12}O_6$; m.p. 161°

In the opinion of other authorities quinic acid is derived from another tetra-hydroxy-hexamethylene in which the two methylenes are in para-position, and not in ortho-position as in fig. 807, and carboxyl has replaced a hydrogen connected with one of the other carbon-atoms.

It is found in quinine bark, bound to lime, and in coffee berries.

## 5. Benzene-acids or Aromatic Acids

A large series of benzene's and its derivatives' combinations with different acids exist, including many important compounds. We can only study a few of the more interesting members, but sufficient to show the red tape running through them all.

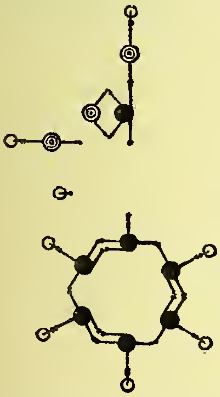
### a. MON-ACID PHENOLS' COMBINATIONS

We commence, then, with *phenol's* (fig. 417, p. 92) combinations with the *fundamental acids* or *benzene's* combinations with *hydroxy-acids* (p. 178), which comes to the same thing when we remember that one molecule of water is separated in both instances, the hydroxyl being taken from that component which has it, and the hydrogen from the other, to form the requisite water. Theoretically both are equally correct, but practically benzenes (particularly those with side-chains) are employed when they are prepared at all in this way.

The first acid is *formic acid* or *carbonic acid*, the latter being considered in this instance hydroxy-formic acid (fig. 690, p. 179).

The formation in both ways may be represented thus:

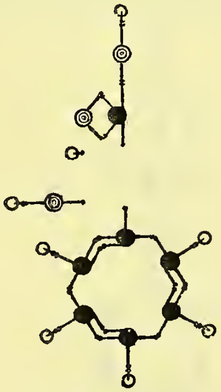
Fig. 810



Carbonic acid and benzene

or

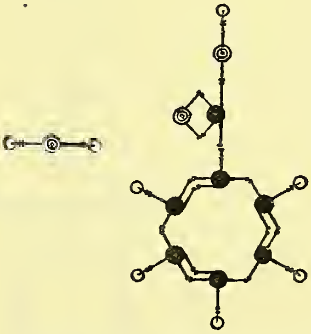
Fig. 811



Formic acid and phenol

=

Fig. 812

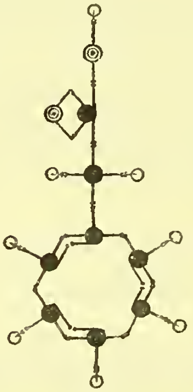


Benzoic acid, $C_7H_6O_2$; m.p. 121°·4

Benzoic acid occurs in gum benzoin, dragon's blood, Peru- and Tolu-balsam, castoreum, cranberries, &c. For medical use it should be prepared from benzoin by sublimation; for other purposes it is generally prepared from toluene (fig. 232, p. 44) by oxidation or from the urine of horses and cows; antiseptic. Its sodium salt is also employed.

From *phenol* and *acetic acid* or from *benzene* and *glycollic acid* (fig. 691, p. 179), we get phenyl-acetic acid.

Fig. 813

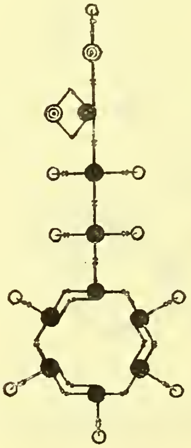


Phenyl-acetic acid, α-toluylic acid, $C_8H_8O_2$ ; m.p. 76°·5 ; used in phthisis and typhus

As the hydroxy-acid always corresponds to the fundamental acid it is unnecessary to specify more than one of them hereafter.

Phenol's combination with *propionic acid* (fig. 669, p. 176)

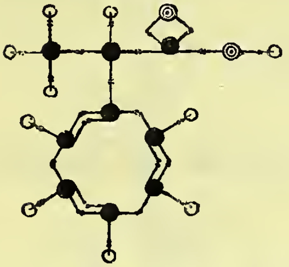
Fig. 814



Hydrocinnamic acid, β-phenyl-propionic acid, $C_9H_{10}O_2$ ; m.p. 48° ; used, like phenyl-acetic acid, in phthisis

From *phenol* and *isoproprionic acid* (so called because the benzene-ring is joined to the intermediate carbon-link. *Vide* isopropyl, fig. 32, p. 11):

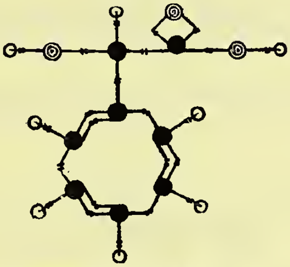
FIG. 815



Hydratropic acid, α-phenyl-propionic acid, $C_9H_{10}O_2$; b.p. 264°

*Phenol* and *glycollic acid* (fig. 691, p. 179)

FIG. 816



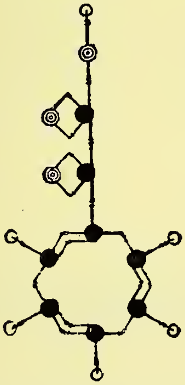
Mandelic acid, phenyl-glycollic acid, $C_8H_8O_3$; m.p. 133°

There are three optically different acids (see lactic acid, p. 179).

For another combination of the two compounds see fig. 917, p. 251.

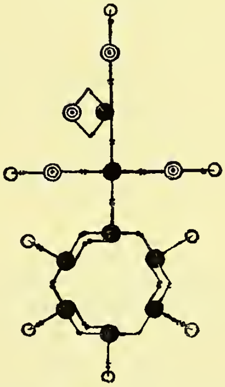
When mandelic acid is cautiously oxidised, the alcoholic carbon is either converted into carbonyl or another hydroxyl is added; probably both forms exist, the former as crystals, the latter as an unstable fluid, which is easily converted into the former.

FIG. 817



Benzoyl-formic acid, $C_8H_6O_3$; m.p. 65°

FIG. 818



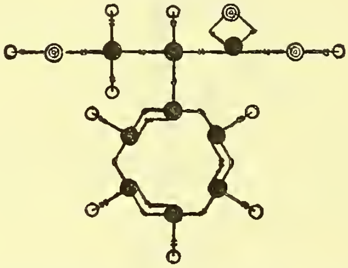
Phenyl-glyoxylic acid, $C_8H_8O_4$; oily liquid

The latter when heated is converted into the solid acid, separating a molecule of water. Benzoyl-formic acid is strictly a ketone-acid (*vide* p. 227).

We have had analogous acids before, viz. glyoxalic acid, fig. 696, p. 180, mesoxalic acid, fig. 729, p. 187 &c.

*Phenol* and *hydracrylic acid* (fig. 693, p. 179)

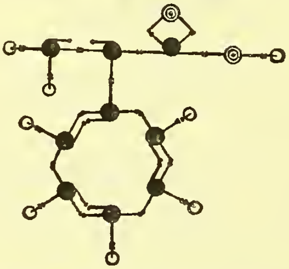
Fig. 819



Tropic acid, α-phenyl-hydracrylic acid, $C_9H_{10}O_3$; m.p. 118°; consists of two stereo-isomeric acids, lævo-acid (m.p. 123°) and dextro-acid (m.p. 128°)

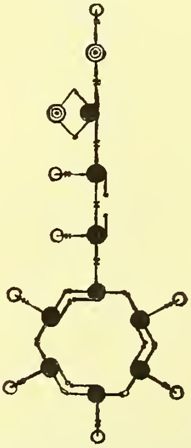
*Phenol* and *acrylic acid* (fig. 738, p. 190) form two isomeric acids:

Fig. 820



1. Atropic acid, α-phenyl-acrylic acid, $C_9H_8O_2$; m.p 106°·5

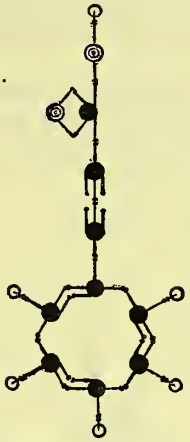
Fig. 821



2. Cinnamic acid, β-phenyl acrylic acid $C_9H_8O_2$; m.p. 133°; used in tuberculosis

*Phenol* and *propiolic acid* (fig. 771, p. 199)

FIG. 822



Phenyl-propiolic acid, $C_9H_6O_2$; m.p. 136°; also derivable from *cinnamic acid* by removing the two hydrogen atoms in the double bond

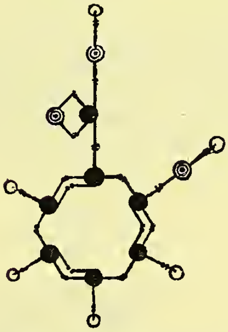
These acids were all formed from mon-acid phenol or carbolic acid; but poly-acid phenols (*vide* p. 92) may also combine with acids, not only by one hydroxyl, but by as many as they are in possession of, each hydroxyl being able to join a separate molecule of acid. Thus we commence with

## b. DI-ACID PHENOLS' COMBINATIONS

### 1. Monobasic Acids

*Di-acid phenol* and *formic acid*:

FIG. 823



Salicylic acid, *o*-hydroxy-benzoic acid, $C_7H_6O_3$; m.p. 155°; occurs in nature in the blossoms of *Spiræa ulmaria*, and in combination with methyl in winter-green oil; powerful antiseptic

Bismuth salicylate, $C_6H_4\left\langle\begin{matrix}COO\\O\end{matrix}\right\rangle Bi.OH$, used in typhoid fever, breaks up in the intestines, but not in the stomach. Bismuth, being a tri-valent metal, displaces the hydrogens, both in carboxyl and in the alcoholic hydroxyl of the salicylic acid. Its third valency is attached to another hydroxyl.

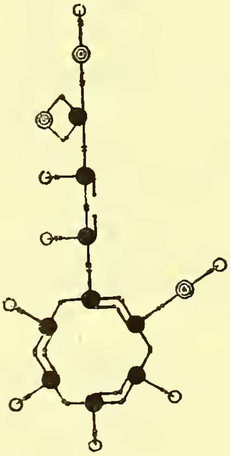
Salicylic acid is derivable from *catechol* (fig. 418, p. 92); the two other isomers, resorcin and hydroquinone, also form acids with a molecule of formic acid, but they have no antiseptic properties. That from resorcin, meta-hydroxy-benzoic acid, has, however, theoretical interest, and therefore been frequently referred to before. The derivative from hydroquinone is termed para-hydroxy-benzoic acid.

Pheno-salyl (*Wiener Med. Bl.* 1893, p. 329) is salicylic, carbolic, and benzoic acids melted together and then dissolved in lactic acid with addition of a little glycerin to prevent crystallisation. A solution of 1 : 1000 kills cholera bacilli within a minute.

Eulyptol is a mixture of salicylic and carbolic acids with eucalyptus oil.

*Di-acid phenol* and *acrylic acid* (fig. 738, p. 190)

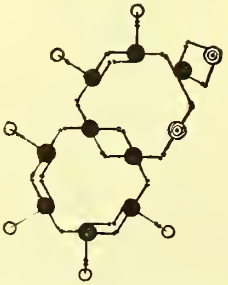
Fig. 824



*o*-Coumaric acid, ortho-hydroxy-cinnamic acid, $C_9H_8O_3$; m.p. 207°; occurs in *Melilotus officinalis*; the *meta-* and *para-*compounds are also known

When two hydroxyls are in positions similar to those above, the chain to which one of them is linked is inclined to bend in order that the two may meet, and, by dropping a molecule of water, unite the open end of the side-chain to the benzene-ring, forming an intramolecular anhydride or lactone. This is the more the case when a pentagon or hexagon can be formed of the side-chain; in coumaric acid the long side-chain and the ortho-position of the hydroxyl favour such a proceeding (see also pp. 182 and 185).

Fig. 825

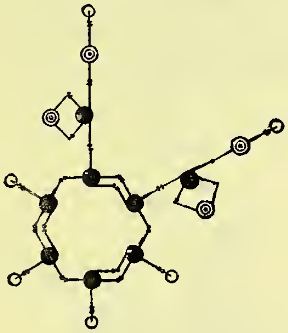


Coumarin, coumaric anhydride, $C_9H_6O_2$; m.p. 67°; occurs in the Tonquin bean, in woodruff (*Asperula odorata*), &c.

## 2. Dibasic Acids

Both hydroxyls of di-acid phenols may be joined by formic acid. From *catechol* is thus formed ortho-benzene di-carboxylic acid, or phthalic acid:

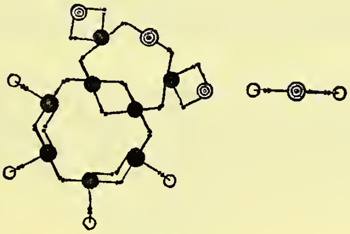
Fig. 826



*o*-Phthalic acid, $C_8H_6O_4$; m.p. 184°–213°

The positions of hydroxyls are also here favourable to forming an anhydride (see above).

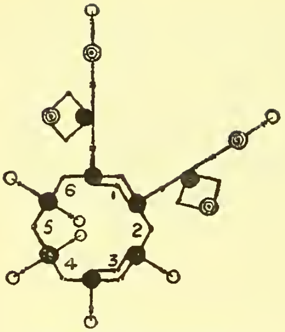
Fig. 827



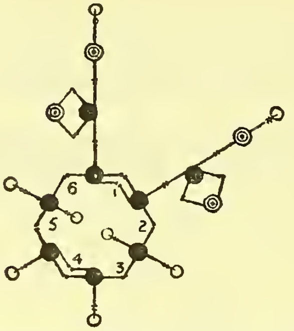
Phthalic anhydride, $C_8H_4O_3$; m.p. 128°

From *resorcin* (fig. 419, p. 92) is derivable a meta-, and from *hydroquinone* (fig. 420, p. 92) a para-phthalic acid. The former is also termed isophthalic acid (1 : 3), m.p. above 300°, and the latter terephthalic acid (1 : 4); sublimes without melting. They do not form anhydrides.

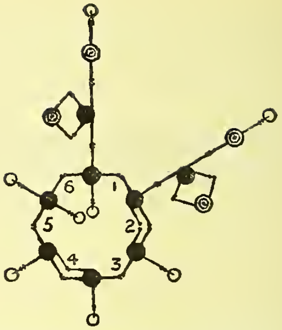
There is only one of each of the three phthalic acids above, but as soon as one or more of the double bonds are broken by the introduction of hydrogen-atoms inside the ring, the door is opened for a crowd of isomers differing in the positions of the double bonds. Thus there are seven isomers of *o*-phthalic acid by the introduction of two hydrogen-atoms, six of them depending upon which double bond is broken, and a seventh which is stereo-isomeric to one of the six. They are all termed di-hydro-phthalic acids, and individually distinguished as explained below.



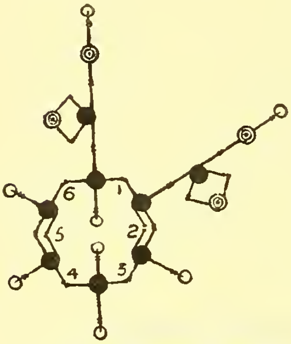
$\Delta^{1\cdot 3}$ di-hydro-phthalic acid



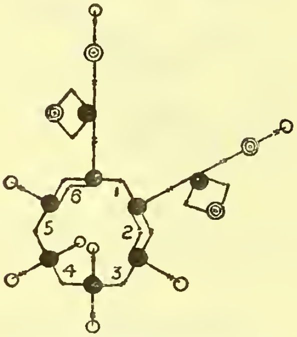
$\Delta^{1\cdot 4}$ di-hydro-phthalic acid; m.p. 153°



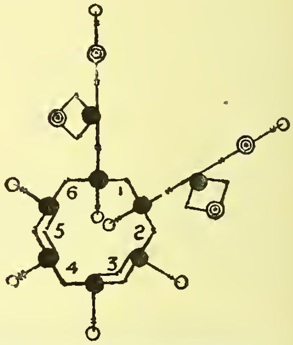
$\Delta^{2\cdot 4}$ di-hydro-phthalic acid; m.p. 180°



$\Delta^{2\cdot 5}$ di-hydro-phthalic acid



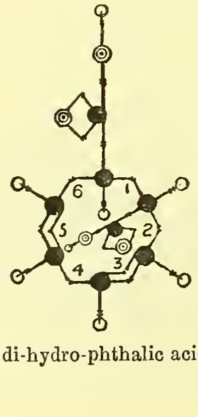
$\Delta^{2\cdot 6}$di-hydro-phthalic acid;
m.p. 215°



*Cis*-$\Delta^{3\cdot 5}$ di-hydro-phthalic acid;
m.p. 175°

The double bonds are indicated by the Greek capital $\Delta$, and their positions by index numerals as shown above. This mode of distinguishing the several isomers of hydrated benzene derivatives is becoming generally adopted.

Two of these acids, $\Delta^{1\cdot 3}$ and $\Delta^{2\cdot 5}$, have not yet been prepared; a stereo-isomer of the last one, $\Delta^{3\cdot 5}$, has, however, been found, the existence of which is in full harmony with the tetrahedron theory (*vide* p. 482), which does not admit stereo-isomers of any of the other di-hydro-phthalic acids. The structure of this seventh isomer may be illustrated in the following way:



*Trans*-$\Delta^{3\cdot 5}$ di-hydro-phthalic acid; m.p. 210°

When both carboxyls are placed on the same side of the ring the compound is designated as a *cis-* or maleïnoïd form; if they are on different sides it is distinguished as a *trans-* or fumaroïd form.

There are six tetra-hydro-phthalic acids, $\Delta^1$, $\Delta^2$, *cis*-$\Delta^3$, *trans*-$\Delta^3$, *cis*-$\Delta^4$, and *trans*-$\Delta^4$: all of them have been prepared, likewise the two possible (*cis-* and *trans-*) hexa-hydro-phthalic acids.

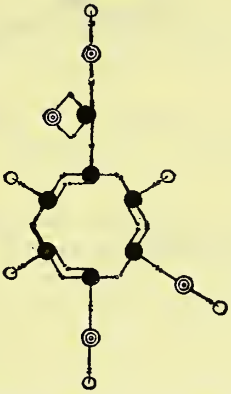
Altogether twenty-three hydro-phthalic acids have been prepared.

## c. TRI-ACID PHENOLS' COMBINATIONS

*Tri-acid phenol* and *formic acid*:

Six different combinations are possible between the three tri-acid phenols and a molecule of formic acid, and they are all known. We shall mention one of them.

Fig. 828

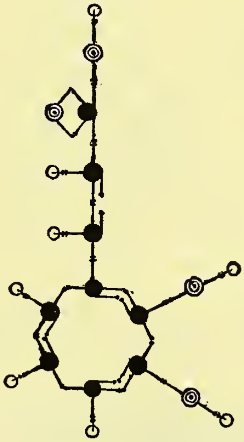


Proto-catechuic acid, $C_7H_6O_4$; m.p. 199°

All the hydroxyls in each of the three phenols can combine with formic acid, forming three different acids: trimesic acid (1 : 3 : 5, *vide* p. 43), m.p. above 300°; trimellitic acid (1 : 2 : 4), m.p. 216°; and hemimellitic acid (1 : 2 : 3), decomp. on heating. They are, of course, tribasic acids.

*Tri-acid phenol* and *acrylic acid*:

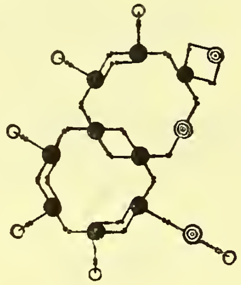
Fig. 829



Di-hydroxy-cinnamic acid, $C_9H_8O_4$

This acid has not been prepared in the isolated state. For the same reason as mentioned under coumaric acid (p. 216), it forms at once an anhydride:

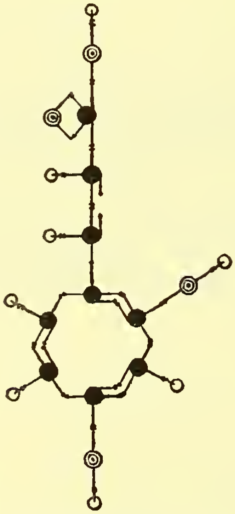
Fig. 830



Di-hydroxy-cinnamic anhydride, $C_9H_6O_3$; m.p. 280°

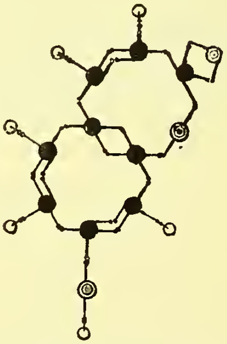
Another of these acids is umbellic acid, with hydroxyls in position 2 : 4 (*vide* p. 43). It forms, therefore, easily, an anhydride, umbelliferone:

Fig. 831



Umbellic acid, $C_9H_8O_4$

Fig. 832

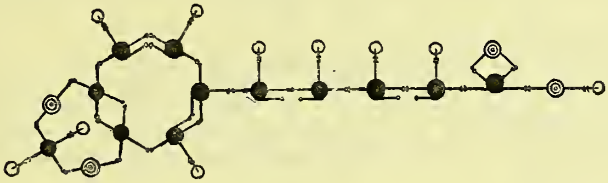


Umbelliferone, $C_9H_6O_3$; m.p. 223°

A third acid is caffeïc acid, $C_9H_8O_4$, which has its hydroxyls in positions 3 : 4, and, therefore, does not form an anhydride.

Finally an acid must be mentioned which is rather unique, in so far as both its components are hypothetical bodies, the phenol-component being an anhydride of *hydroxy-hydroquinone-methyl-ether* (fig. 507, p. 121), and its acid-component a *di-vinyl-carboxylic acid*:

FIG. 833



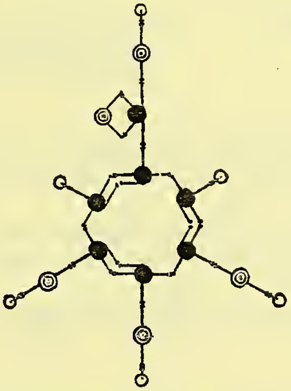
Piperic acid, $C_{12}H_{10}O_4$; m.p. 212°; a decomposition product of piperine (fig. 1431, p. 397); compare also safrol (fig. 504, p. 120), apiol (fig. 506, p. 121), and piperonal (fig. 564, p. 137)

## d. TETRA-ACID PHENOLS' COMBINATIONS

*Tetra-acid phenol* and *formic acid*:

There are three or four known out of a possible six acids; as already explained, they may be considered as derivatives either of *tetra-acid phenols* and *formic acid*, or of *tri-acid phenols* and *carbonic acid.* From the latter point of view they have frequently derived their names; thus the name of one of these acids is pyrogallol-carboxylic acid; another is termed phloroglucin-carboxylic acid; and a third, hydroxy-quinol-carboxylic acid, not yet isolated. The fourth and most important has no systematical name because it was known long before the law of the linking of atoms was thought of: it is gallic acid, 1 : 3 : 4 : 5 (carboxyl being = 1).

FIG. 834



1:3:4:5 Gallic acid, $C_7H_6O_5$; decomposes on heating; occurs in nutgalls, tea, claret, &c.

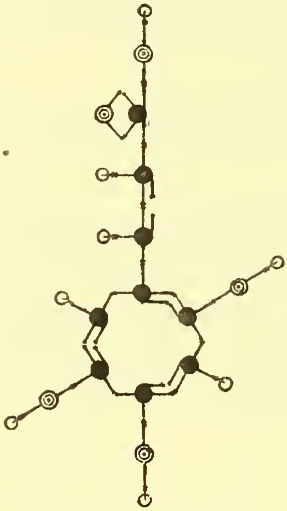
Pyrogallol-carboxylic acid has the structure ($CO_2H=1$) 1 : 2 : 3 : 4, phloroglucin-carboxylic acid, 1 : 2 : 4 : 6. For hydroxy-quinol-carboxylic acid there are three structures to choose from; which of them is the right one is not decided.

*Basic bismuth gallate*, containing 51·29–56·14 per cent. bismuth oxide (besides 1·39 per cent. lead oxide, at least in one sample according to analysis, *Ph. Ztg.* 1892, p. 1) is, under the name of dermatol, recommended as a drying antiseptic, and has recently been used internally with advantage for diarrhœa in phthisis, typhus, malaria, and as a local anæsthetic (*Int. klin. Rundsch.*). The formula $C_6H_2(OH)_3CO_2Bi(OH)_2$ corresponds to 57·7 per cent. $Bi_2O_3$ (Bi=208).

*Tetra-acid phenol* and *acrylic acid* :

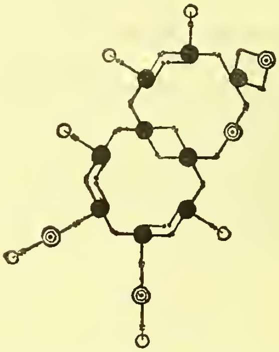
An acid belonging to this series which has the name of æsculetic acid, because its anhydride is named æsculetin, has not been prepared yet in isolated state, but some of its ethers have. One of its hydroxyls is in ortho-position to the carboxyl of acrylic acid, and it forms anhydride like so many of the acids just mentioned. The positions of the two other hydroxyls are 4 : 5.

Fig. 835



Æsculetic acid, $C_9H_8O_5$

Fig. 836



Æsculetin, $C_9H_6O_4$ ; m.p. above 270° ; exhibits in solution a powerful fluorescence ; occurs partly as such, partly as a glucoside, in the bark of *Æsculus hippocastanum*

When the two last-named hydroxyls are in positions 3 : 4, instead of 4 : 5, as in æsculetin, we have a similar anhydride called daphnetin, which occurs as a glucoside in the bark of *Daphne alpina*.

*Tetra-acid phenol's* four hydroxyls can each combine with *formic acid*, producing benzene-tetra-carboxylic acid. In the same manner *penta-* and *hexa-acid phenols* form benzene-penta- and hexa-carboxylic acids.

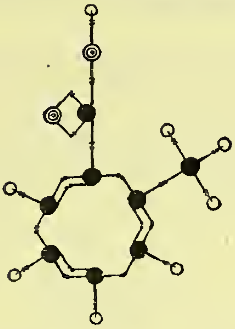
This last one is termed mellitic acid, $C_{12}H_6O_{12}$, occurring as aluminium-salt in honey-stone.

## e. MON-ACID TOLUENE PHENOLS' COMBINATIONS

### *with formic acid*

Three acids corresponding to the three cresols (figs. 428–430, p. 95) are known. The illustration of one of them will suffice :

FIG. 837



Ortho-toluic acid, $C_8H_8O_2$; m.p. 102°·5

## f. DI-ACID TOLUENE PHENOLS' COMBINATIONS

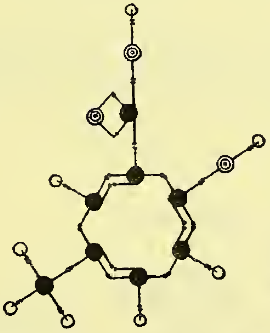
*with formic acid*

From the six possible *di-acid toluene-phenols* (p. 96) ten different acids may be formed, and we know them all. They are distinguished by the common name cresotic acids, or systematically hydroxy-toluic acids; singly they enjoy rather long names, which it would be purposeless to specify here. It may, however, be deemed interesting to see how so many different compounds can be arranged with the three groups, carboxyl, hydroxyl, and methyl; therefore I give the figures representing their respective places on the benzene-ring in the order just enumerated:

1 : 2 : 3 ... 1 : 2 : 4 ... 1 : 2 : 5 ... 1 : 2 : 6 ... 1 : 3 : 2 ... 1 : 3 : 4
1 : 3 : 5 ... 1 : 4 : 2 ... 1 : 4 : 3 ... 1 : 5 : 2

Here is an illustration of one of them:

FIG. 838



Para-homosalicylic acid, α-cresotic acid, or ortho-hydroxy-meta-toluic acid, $C_8H_8O_3$; m.p. 151°; used in *articular rheumatism, typhus, pneumonia,* &c., in children; not poisonous

Solutions of cresols in these acids or in their sodium-salt are known as lysol and solutol (*vide* p. 96).

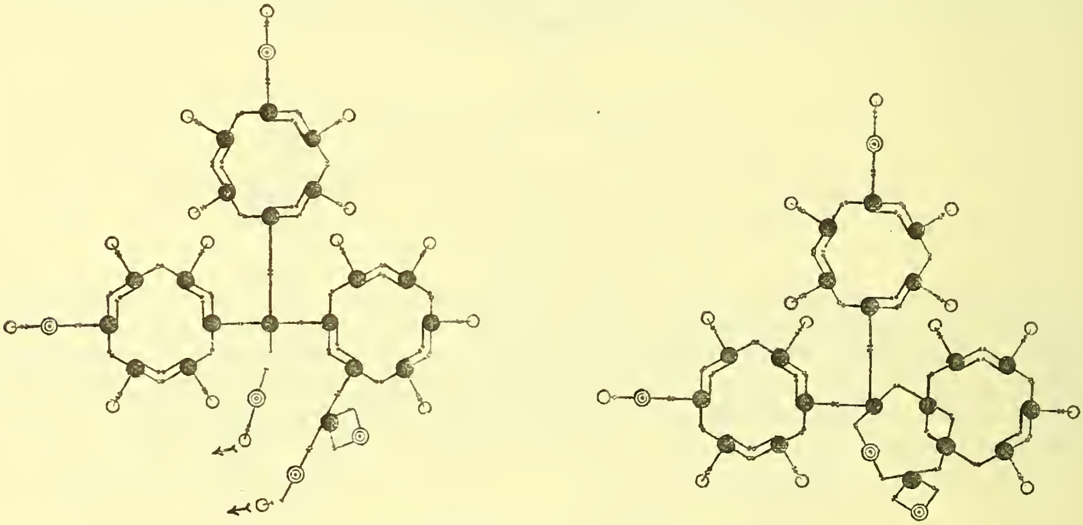
It is not only the true phenols that form acids in this way; any phenol-compounds which have a hydroxyl free to join an acid can do so. Of such phenol-compounds we can mention phenol-alcohols (p. 106), and will give a few useful examples:

## g. PHENOL-ALCOHOLS' COMBINATIONS

*Tri-phenol carbinol* (fig. 466, p. 107) unites with *formic acid*, or *phenyl-di-phenol-carbinol* (fig. 465, p. 107) with *carbonic acid*, forming an acid that has not yet been isolated, because the carboxyl goes from para- into ortho-position, and joins the alcoholic hydroxyl, separating a molecule of water and forming an anhydride (*vide* p. 108).

Fig. 839

Fig. 840

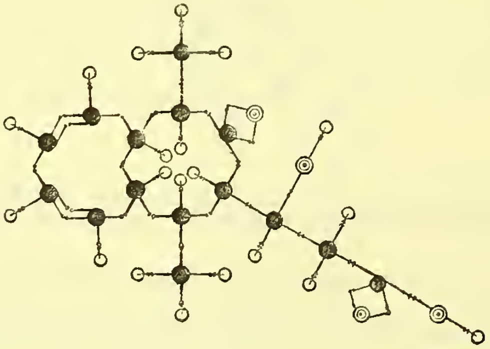


Phenolphthaleïn, $C_{20}H_{14}O_4$; m.p. 250°

The smallest trace of an alkali colours its solution a magnificent pink, and acids, but not carbon di-oxide, destroy the colour. It is therefore one of the finest indicators of neutrality, especially for such acids as palmitic, stearic, oleïc, &c.; it cannot, however, be employed in the presence of ammonium-salts.

Naphthalene-phenols similarly combine with acids. We are interested in only two of these compounds, santoninic acid and santonin. They have up to quite recently been regarded as hydrated (*vide* p. 33) oxy-di-methyl-naphthol's (*vide* fig. 453, p. 103) combination with hydracrylic acid (*vide* fig. 693, p. 179).

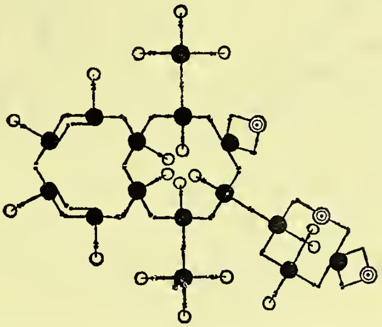
Fig. 841



Santoninic acid, $C_{15}H_{20}O_4$; sodium santonate is a vermifuge

On heating it forms a lactone (p. 182), the carboxylic and alcoholic hydroxyls in the side-chain uniting by the separation of a molecule of water and forming (*Ber.* xviii. p. 2748)

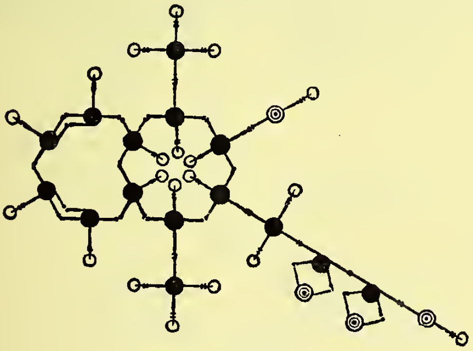
Fig. 842



Santonin, $C_{15}H_{18}O_3$; m.p. 170°; anthelmintic

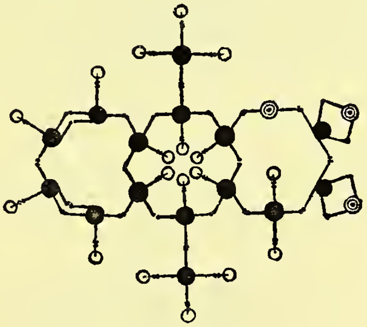
But, according to later researches (*Ber.* xxv. p. 3318 and xxvi. pp. 411, 786, April 1893), this structure is incorrect. In the opinion of one authority these compounds are to be looked upon as a combination of a *hydrated β : β-di-hydroxy-naphthalene* with *pyroracemic acid* (fig. 851, p. 227). The consequence as regards the structure is that the hydroxyl of the side-chain takes the place of carbonyl (the ketone index) in the naphthalene-ring, while the latter goes into the side-chain. A further consequence is that the formation of santonin is not a performance exclusively in the side-chain, as represented above, but an operation in which the naphthalene-ring takes a part through its hydroxyl by the formation of three interlocked benzene-rings. The two compounds interpreted in this way would, therefore, have such structures:

Fig. 843



Santoninic acid

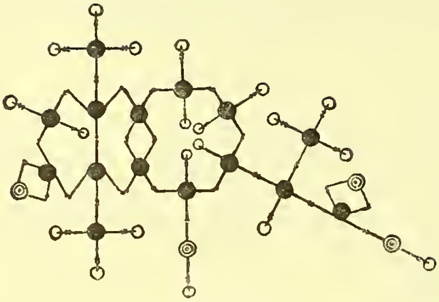
Fig. 844



Santonin

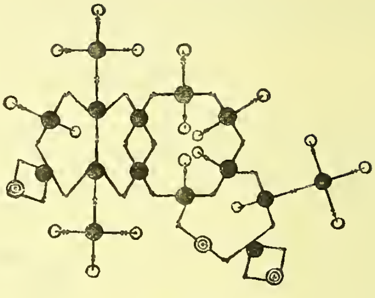
In the opinion of the other authority the two compounds are somewhat related to terpenes, or, better still, a combination of *naphthalene*-formed *terpene* with *iso-propionic acid*:

Fig. 845



Santoninic acid

Fig. 846



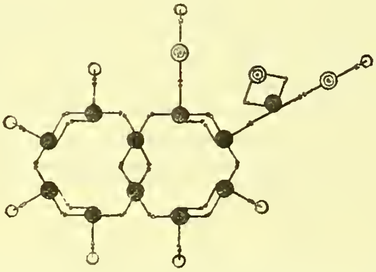
Santonin

## h. DI-HYDROXY-NAPHTHALENES' (β-Naphthol-quinol, fig. 455, p. 104) COMBINATIONS

*with formic acid*

Out of fourteen possible isomers eight have been prepared, one of which is

Fig. 847



α-Hydroxy-naphthoïc acid, α-naphthol-carboxylic acid, α-oxy-naphthoïc acid, $C_{11}H_8O_3$; m.p. 185°; more powerful antiseptic than salicylic acid, and a very effective antizymotic and antipyretic (in fever internally, but with caution, as it is poisonous; in diseases of the skin—scabies, prurigo—externally); used, under the name of sternutament, as snuff for nasal catarrh

# B and C. ALDEHYDE- AND KETONE-ACIDS

When formic acid through its carboxyl (or an aldehyde through its alkyl) joins the alkyl-part of another acid, aldehyde acids are formed; *any other than formic acid* produces ketone acids.

Excepting formic acid itself, which may be looked upon as the first member of this class, the first of the aldehyde-acids is formed from two molecules of formic acid, viz. glyoxalic acid, which has already been mentioned under di-hydroxy-acids of the fundamental series (fig. 697, p. 181), and we will therefore commence by joining formic and acetic acids in the way mentioned, producing the next aldehyde-acid, i.e. a compound which is acid at one end and aldehyde at the other.

Fig. 848

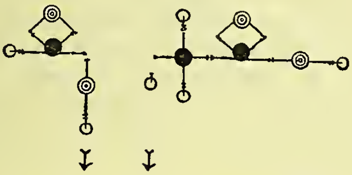


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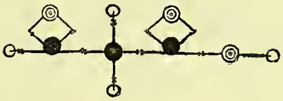
Fig. 849



Formic acid + acetic acid

Formyl-acetic acid, $C_3H_4O_3$; easily oxidised to malonic acid (fig. 713, p. 184)

Owing to the peculiar structure of formic acid in having no alkyl-body, but being itself aldehyde at one end and acid at the other, it would naturally form aldehyde-acid in the same way from all other acids if capable of existence; they are, anyhow, not known; but not so when formic acid is converted into a higher homologue with alkyl-body by substituting a hydrocarbon-radical for its hydrogen—methyl, for instance, converting formic acid into acetic acid (*vide* p. 175). Therefore if we join acetic instead of formic acid to another acid we obtain a compound which has not an aldehyde in its body, but a ketone (p. 138); for instance:

Fig. 850

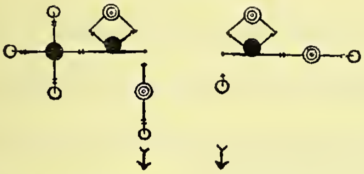


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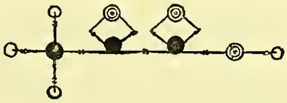
Fig. 851



Acetic acid + formic acid = Pyro-racemic acid, $C_3H_4O_3$; b.p. 165°

Fig. 852

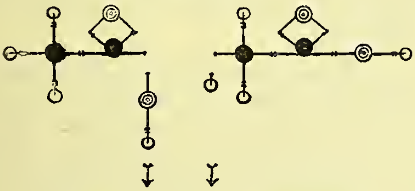


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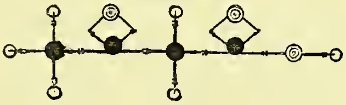
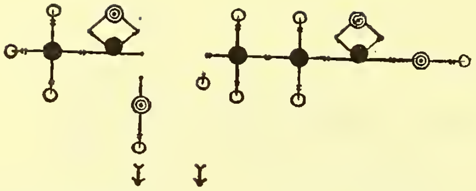
Fig. 853



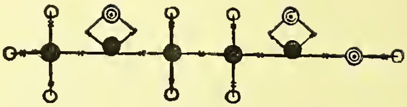
Acetic acid + acetic acid = Aceto-acetic acid, $C_4H_6O_3$; decomposes below 100° is found in urine in *diabetes mellitus*

Fig. 854



Acetic acid + propionic acid

Fig. 855



Levulinic acid, β-acetyl-propionic acid, $C_5H_8O_3$; m.p. 33°·5

There are many more of this series, but the three above are some of the better known compounds.

The structure of aceto-acetic acid, which differs in some respects from the rest, has been very much discussed. It seems as if the structure were *labile*, i.e. that it assumes different forms according to circumstances: we have seen instances of this before (glyoxalic acid, fig. 696, p. 180, and mesoxalic acid, fig. 729, p. 187; compare also what is said about the double bond in benzene, p. 54). Through being enclosed between two carbonyls (ketone-index), methylene is equally attracted to both, swinging to and fro like a pendulum. If, now, anything happens to lessen the attention which one of the carbonyls is paying to the hydrogen in the methylene-group (and this will occur from the attachment of something very attractive to the carboxyl-group), then the other carbonyl gets the advantage of the hydrogen which jumps over to the oxygen, whereby two valencies are released, and join each other forming a double-bond.

Fig. 856

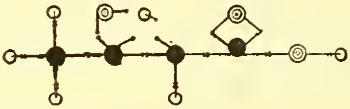
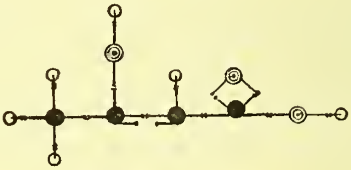


Fig. 857



This is termed the alcoholic form of aceto-acetic acid, whereas the former is the ketonic form.

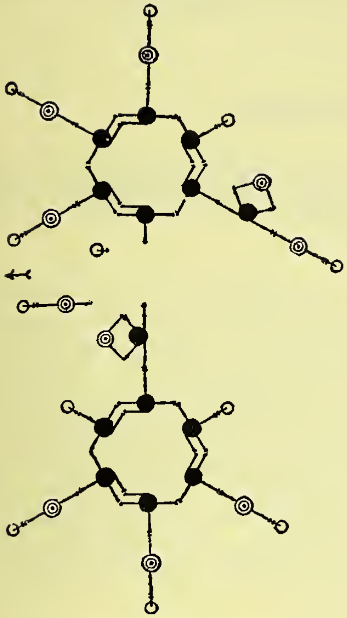
Some chemists will, of course, not admit this duplicity of the hydrogen, and stick to the ketonic form through thick and thin.

The two other ketonic acids with no such vacillating hydrogen, having either two hydrogens or none at all between the two carbonyls, are beyond suspicion and doubt.

Another remarkable property of aceto-acetic acid, or practically its ethers (*vide* p. 232), is that the hydrogens of methylene can be replaced by alkali-metals (but only one at a time), alcohol-radicals, acid-radicals, and elements and groups, some of which will be subsequently mentioned, *e.g.* iso-nitroso-group, imido-group, chlorine, &c. That makes the acid one of the most useful compounds in chemical synthesis.

There is still a group of ketone acids which should not escape our attention, the tannic acids, prepared from the various barks. Some of the tannic acids appear to be glucosides (gummides, dextrides), but the oak-tannic acids are, according to the latest researches (*Monatsh.* x. p. 647), ketone acids, formed from the *carboxyl* of one molecule of gallic acid (fig. 834, p. 221) joining a *benzene-hydrogen* of another molecule of the same acid, separating, of course, a molecule of water.

Fig. 858



Two molecules of gallic acid

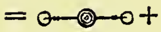
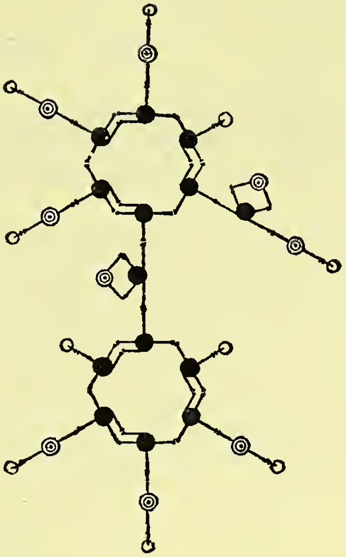


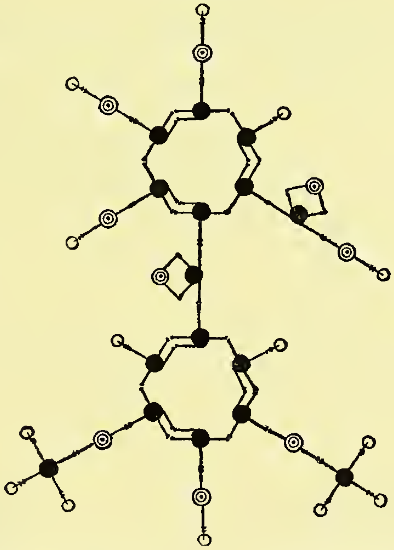
Fig. 859



Oak-tannic (querci-tannic) acid, $C_{14}H_{10}O_9$

There are several homologues of the acid according to the different varieties of oak from which they are prepared. Their differences consist in the etherification of the acids by the joining of methyl to the phenol-hydroxyls:

Fig. 860



Oak-tannic acid, $C_{16}H_{14}O_9$; with two methoxyls

There are acids with four methoxyls, $C_{18}H_{18}O_9$, and with six methoxyls, $C_{20}H_{22}O_9$

The tannic acids are, of course, used for tanning, and in this respect, as also in structure, are distinguished from tannin, which is a compound-ether-acid (fig. 926, p. 255).

## D. KETONE-ALDEHYDES

being, at present, of little interest from a therapeutical point of view, the description of their formation given on p. 207 will suffice, and we can pass on to consider the combinations of acids and alcohols, or phenols—the compound ethers.

# E. COMPOUND ETHERS, NEUTRAL AND ACID

(ESTERS AND ESTER-ACIDS)

When acids combine with alcohols or phenols through their carboxyl- and hydroxyl-parts they are termed ethers on account of their analogy to the true ethers (p. 113), both in their formation and in many physical properties. The ethers were formed from *two alcohols* (or phenols), joining under separation of a molecule of water; the compound ethers are formed from an *alcohol* (phenol) joining an *acid* under the same condition. In the case of polybasic acids as many molecules of (the same or different) alcohols may join as there are carboxyls with which to effect a union. When all carboxyls are thus engaged neutral compound ethers are formed: if not, they are acid compound ethers. Compound ethers are by German chemists distinguished as 'esters.'

There are a great many compound ethers; we can only reproduce a few of them, limiting ourselves to those that are typical or possess some interest to the reader.

We may classify them into combinations of

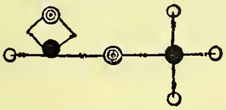
Aliphatic Acids with Alcohols
,, ,, ,, Phenols
Cyclo-acids ,, Alcohols
,, ,, Phenols

## I. Aliphatic Acids and Alcohols

### a. MONOBASIC ACIDS AND MONACID ALCOHOLS

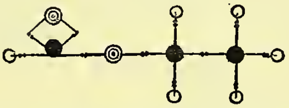
These ethers possess for the most part a pleasant fruity smell.

FIG. 861



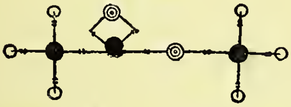
Methyl-formate, $C_2H_4O_2$; b.p. 32°·3; occurs in crude wood-spirit

FIG. 862



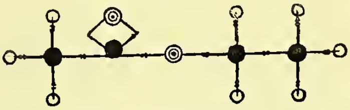
Ethyl-formate, $C_3H_6O_2$; b.p. 54°·4; used in the artificial preparation of rum and arrack

FIG. 863



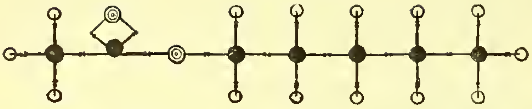
Methyl-acetate, $C_3H_6O_2$; b.p. 57°·5; occurs in crude wood-spirit

FIG. 864



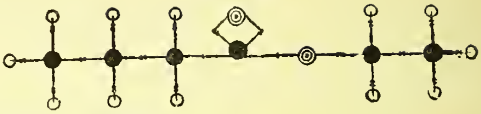
Ethyl-acetate, acetic ether, $C_4H_8O_2$; b.p. 77°

FIG. 865



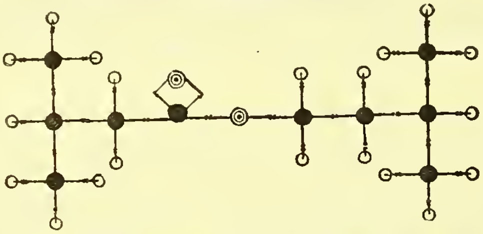
Amyl-acetate, $C_7H_{14}O_2$; b.p. 148°; smell of jargonelle pears

FIG. 866



Ethyl-butyrate, $C_6H_{12}O_2$; b.p. 121°; smell of pineapples

FIG. 867



Iso-amyl-iso-valerate; b.p. 196°; smell of apples

What is called '*bouquet*' in wine, or *œnanthether*, is a mixture of ethyl-, œnanthyl-, caprylyl-, pelargonyl-, and capryl-ethers at the ratio of 1 to 40,000 parts of wine.

The fruit essences are artificial mixtures of these ethers; perhaps the composition of some of them may interest.

| | | |
|---|---|---|
| Apple | Essence: | iso-amyl-iso-valerate |
| Apricot | ,, | amyl-butyrate |
| Cherry | ,, | ethyl-acetate and benzoate |
| Cognac | ,, | ethyl-acetate and nitrite |
| Melon | ,, | ethyl-sebacate |
| Mulberry | ,, | ethyl-suberate |
| Pear | ,, | iso-amyl-acetate and ethyl-acetate (10 : 1) |
| Pineapple | ,, | ethyl-butyrate |
| Quince | ,, | ethyl-pelargonate |
| Rum | ,, | ethyl-formate mixed with some other ethers |
| Strawberry | ,, | ethyl-acetate and butyrate, and iso-amyl-acetate |

(*Beilst*, i. p. 426.)

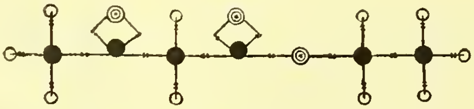
Amongst the compound ethers of the higher alcohols and fatty acids may be mentioned:

| | | |
|---|---|---|
| Cetyl-palmitate, | $C_{15}H_{31}$ CO-O-$C_{16}H_{33}$, | the chief constituent of spermaceti |
| Melissyl- (myricyl-) palmitate, | $C_{15}H_{31}$ CO-O-$C_{30}H_{61}$, | in bees-wax, Ceylon and Carnauba wax |
| Ceryl-cerotate, | $C_{26}H_{53}$ CO-O-$C_{27}H_{55}$, | occurs in Chinese wax |

The structures of compound ethers formed from other than fundamental acids are in every way analogous to the above.

One of them is worth mentioning because of its ability to unite with other compounds, and afterwards to split up in different ways, wherefore it is being largely used in modern synthetical processes. It is the combinations in ether-fashion of *aceto-acetic acid* (fig. 853, p. 227) and *alcohols*, the aceto-acetic ethers:

FIG. 868

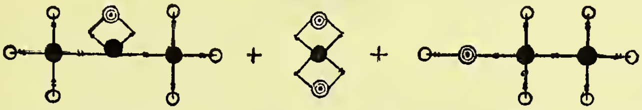


Aceto-acetic ethyl-ether, $C_6H_{10}O_3$; b.p. 181°

The two methylene-hydrogens between the carbonyls may be replaced by various substitutes mentioned under aceto-acetic acid, p. 228.

It is split up in two ways, according to the reagents employed: one is termed ketonic decomposition:

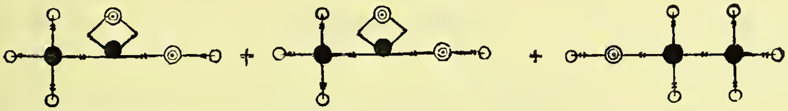
Fig. 869



Aceton (comp. fig. 566, p. 138) + Carbon dioxide (fig. 711, p. 184) + Ethyl alcohol (fig. 337, p. 70)

The other is termed acid decomposition:

Fig. 870



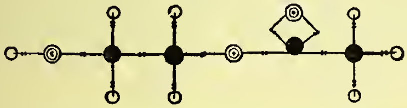
Two molecules of acetic acid (fig. 667, p. 175) + Ethyl alcohol

For its behaviour in other respects compare what is said about aceto-acetic acid, p. 228.

## b. MONOBASIC ACIDS AND POLYACID ALCOHOLS

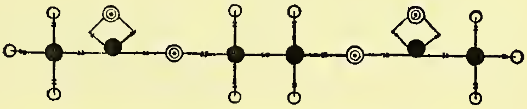
The polyacid alcohols can join an acid to every one of their alcoholic hydroxyls; *e.g.* glycol (fig. 364, p. 76) has two hydroxyls of which one or both may be joined to acetic acid

Fig. 871



Ethylene-monacetate or ethylene monacetin, $C_4H_8O_3$; b.p. 182°

Fig. 872



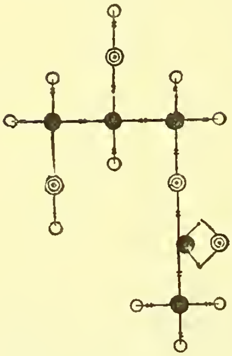
Ethylene-diacetate or ethylene diacetin, $C_6H_{10}O_4$; b.p. 186°

but they are not of much consequence until we come to glycerin (fig. 375, p. 78), which forms with the higher homologues of the aliphatic acids some of the most widely spread compounds in nature, the fats.

Glycerin combines with the higher homologues of the aliphatic acids exactly in the same way as with the lower homologues; therefore a few examples of the last will serve as an introduction to the more important compounds. On account of their many analogies and their great importance as a class, their names have been fashioned in one mould, the suffix '-ate' of the acid being changed to '-in,' and mono-, di-, or tri- prefixed to indicate how many molecules of acid have entered into the compound; *e.g.* mon-acetin, di-acetin, and tri-acetin, &c. As a class they are all termed glycerides, distinguished as mono-, di-, or tri-glycerides.

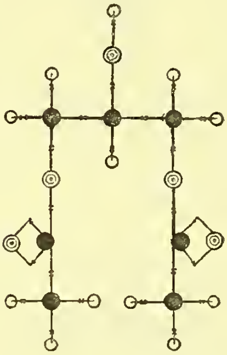
*Glycerin's* combinations with *acetic acid* are

Fig. 873



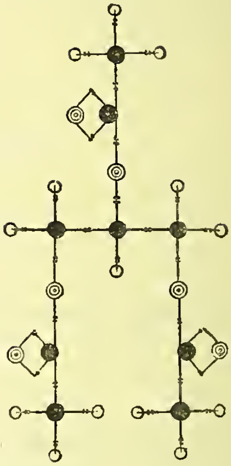
Monacetin, $C_5H_{10}O_4$; b.p. not stated; mono-glyceride

Fig. 874



Diacetin, $C_7H_{12}O_5$; b.p. 280°; an isomer with acetyl in $\beta$-position has b.p. 250°; di-glyceride

Fig. 875



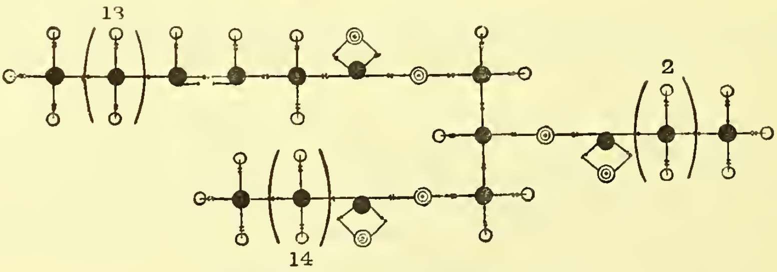
Triacetin, $C_9H_{14}O_6$; b.p. 268°; tri-glyceride

The latter occurs in small quantities in oil from the seeds of *Euonymus europæus*, is said to have been found in cod-liver oil, but probably only as a product of decomposition.

In the same way *glycerin* combines with *butyric-*, *valeric-*, *caproïc-*, *caprylic-*, *capric-*, *lauric-*, *myristic-*, *palmitic-*, *stearic-*, *arachidic-*, and *oleïc-acids*, all of which in the form of tri-glycerides have been found in pure butter; further, with *behenic-*, *lignoceric-*, *erucic-*, *theobromic-*, *hypogæïc-*, *physetoleïc-acids* found in other fats; and *linolic-*, *linolenic-*, and *iso-linolenic acids* in linseed oil; with *ricinoleïc acid* in castor oil, and with *jecoleïc* and *therapic acids* in cod-liver oil, always as tri-glycerides.

Only tri-glycerides are found in nature, except in some more complex compounds where one of the hydroxyls in glycerin is used to connect the glycerides with some other compound (*vide* lecithin, fig. 1536, p. 435). The acids united to one molecule of glycerin in form of compound ethers are usually of the same sort, though not necessarily so; for instance, a tri-glyceride found in butter is an oleo-palmito-butyrin (*Ch. Ztg.* 1889, xiii. p. 128; *Benedikt Fette*, p. 391).

Fig. 876

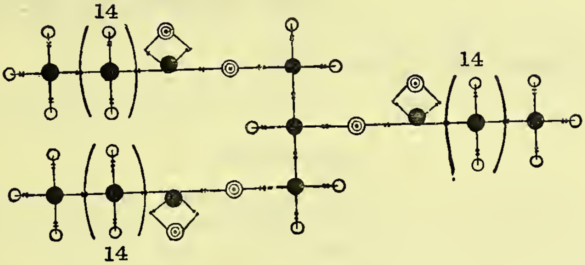


Oleo-palmito-butyrin, $C_{41}H_{76}O_6$; crystals

The most important of these tri-glycerides are

### Palmitin (*tri-palmitin*)

FIG. 877

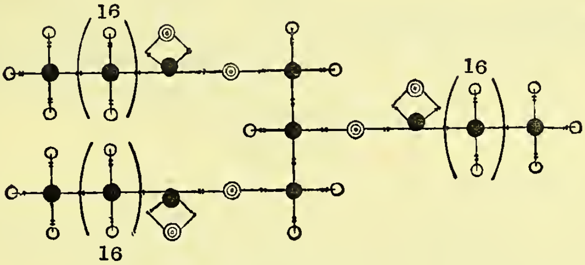


Palmitin, $C_{51}H_{98}O_6$

Palmitin melts first at 50°·5; on further heating it solidifies and melts again at 66°·5, a rather uncommon and remarkable behaviour. (*Benedikt Fette*, p. 36; *Schaedler Technol.* i. p. 154, gives even three different m.p.) It occurs in nearly all fats, but is particularly abundant in palm oil. It is also found in cod-liver oil to the extent of probably less than 5 per cent., retained in solution in the fluid part of oil, even if it has been kept for several days at a temperature of —7° of cold, although palmitin by itself solidifies, as already stated, at a temperature between 50° and 60°

### Stearin (*tri-stearin*)

FIG. 878



Stearin, $C_{57}H_{110}O_6$

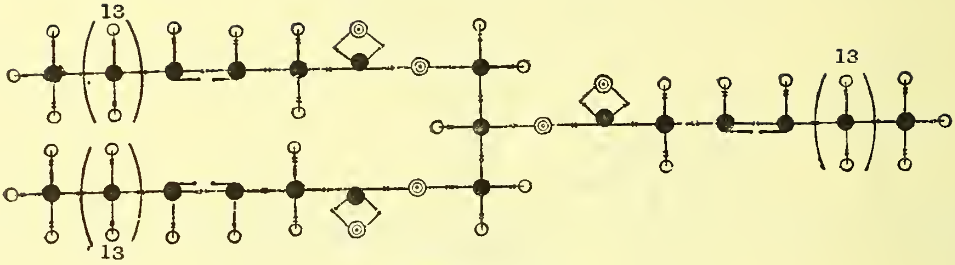
Stearin, like palmitin, melts twice on heating, first at 55°, solidifying on further heating and melting again when the temperature has reached 71°·5.

It occurs in nature nearly always in company with palmitin.

Cod-liver oil on cooling towards the freezing-point throws down a crystalline mass which has hitherto been mistaken for stearin. The greater part of it consists of glycerides of unsaturated acids.

### Oleïn (*tri-oleïn*)

Fig. 879



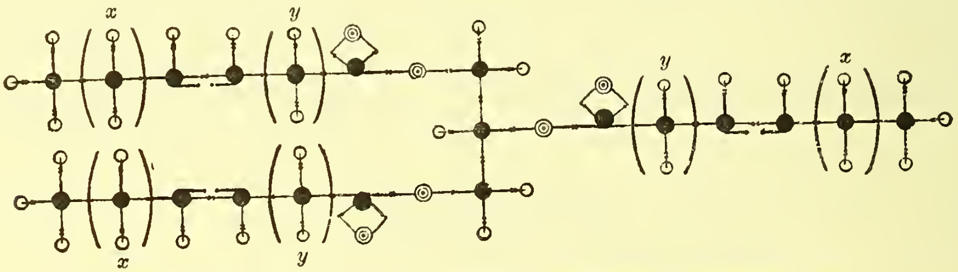
Oleïn, $C_{57}H_{104}O_6$

Oleïn is liquid and solidifies at $-6°$. It is converted by nitrous acid into elaïdin, a solid compound which melts at 44° and possesses the same geometrical structure as oleïn. The difference between them is of a stereometrical nature and fully analogous to that of oleïc- and elaïdic-acid or erucic- and brassidic-acid (*vide* pp. 190, 191).

Oleïn is widely distributed in nature. There are very few fats which do not count it amongst their constituents.

### Jecoleïn (*tri-jecoleïn*)

Fig. 880

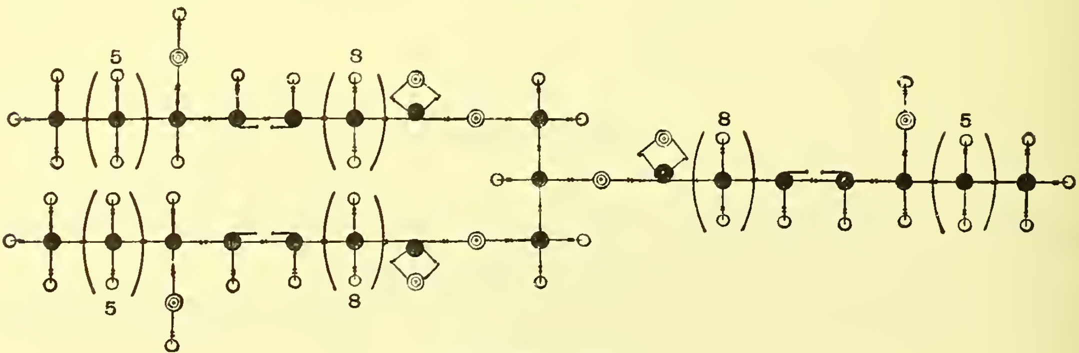


Jecoleïn, $C_{60}H_{110}O_6$; $x+y=15$; $y$ is probably a considerably higher figure than $x$

Jecoleïn, recently found by Heyerdahl in cod-liver oil, is one of the constituents of that part of the oil which has hitherto been taken to be exclusively oleïn. It is present in the oil to the extent of about 20 per cent.

### Ricinoleïn (*tri-ricinoleïn*)

Fig. 881

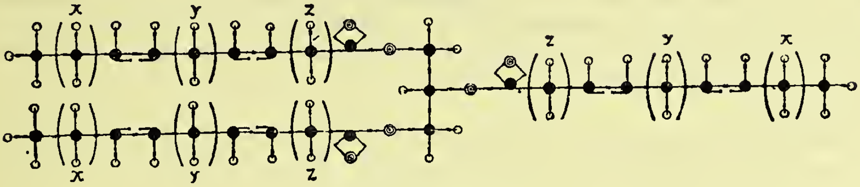


Ricinoleïn, $C_{57}H_{104}O_9$

It appears that castor oil contains two isomeric ricinoleïns, one fluid, the other solid. Neither of them has been isolated free from impurities.

## Linolin

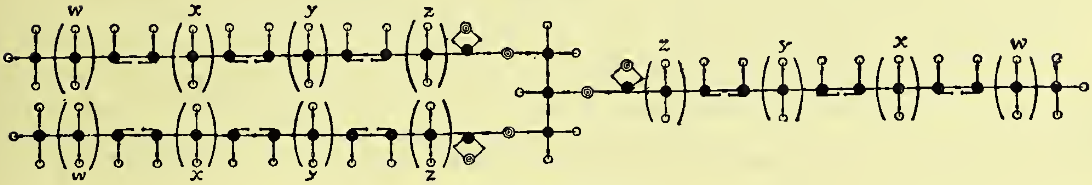
Fig. 882



Linolin $C_{57}H_{98}O_6$

## Linolenin

Fig. 883

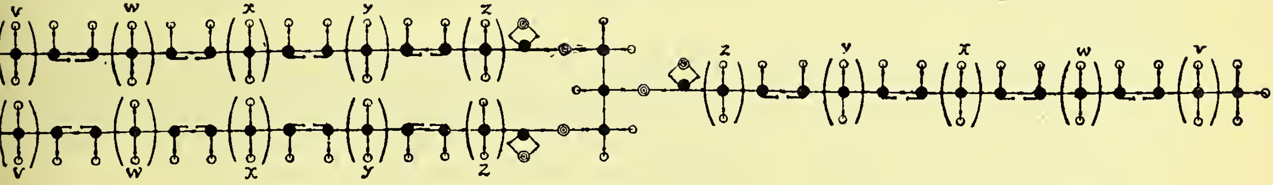


Linolenin, $C_{57}H_{92}O_6$

were until recently considered one compound, *linoleïn*. They occur in linseed oil.

## Therapin

Fig. 884



Therapin, $C_{54}H_{80}O_6$

Therapin has been found in cod-liver oil only, and is without doubt one of the active principles of that valuable remedy. It is present to the extent of 20 per cent. in cod-liver oil, but has not been isolated in a pure state, as it decomposes with such extreme ease. Together with jecoleïn and some other not yet known glycerides, it has, until now, been mistaken for oleïn.

## FATS

The natural fats consist almost exclusively of the tri-glycerides which we have just been discussing. Most of them contain palmitin, stearin, and oleïn in varying proportions. Some are solid because their chief constituents are palmitin and stearin; others are fluid when oleïn is predominant. Some originate in the vegetable world, others are animal fats.

All vegetable fats seem to contain some linolin, of which animal fats are entirely free (*Monatsh.* x. p. 190 &c.).

Palm oil and cacao-butter are solid vegetable fats, the former containing free palmitic acid besides the glycerides.

The fluid vegetable fats are oils of which some, by the action of air, are transformed into a solid substance, and others are not. The former are termed 'drying oils,' and owe their property to a preponderance of linolin and linolenin in their constitution. The principal drying oil is *linseed oil*; others are *poppy*, *hemp*, and *walnut oils.* Of the non-drying oils there are *cotton oil*, *almond oil* (which contains exclusively oleïn and a little linolin, but no saturated acids), *olive oil*, *rape oil*, *sesam oil*, and *castor oil.*

Solid animal fats are numerous, as everyone knows. We have already been informed, p. 234, of the complex constitution of *butter*; *goose-fat* is palmitin, stearin, and oleïn with glycerides of the same volatile acids as in butter, for which it therefore sometimes serves as a substitute on bread. *Mutton-suet* is essentially stearin with a small percentage of palmitin and 25 per cent. of oleïn; *beef-suet* has the same amount of oleïn as mutton-suet, but more palmitin. *Lard* has 60 per cent. of oleïn, and the rest is palmitin and stearin. *Human fat* in infants has three times as much palmitin and stearin as the fat of grown-up people, and one-third less oleïn: that accounts for our own flabbiness, whilst our babies are plump bonny little beauties.

*Oleo-margarin* or artificial butter is prepared from various sorts of tallow carefully melted with water and potash; and after being cooled, subjected to hydraulic pressure at a temperature of 20–22°. That portion which goes through the press at this temperature is oleo-margarine, which is then heated with milk and agitated or churned just like ordinary butter. Some butter-colour and perfume (butyric ether and coumarin) put on the finishing touch. What remains in the press is stearin, used for candle-making.

There are two kinds of animal oils: *blubber-oils* and *liver-oils.* Some of the former are *seal-oil* from different species of *Phoca*, *whale-oil* from whales, *bottlenose-oil* from *Delphinus globiceps*, *porpoise-oil* from *Delphinus phocæna* (contains 10 per cent. or more of valeric acid), *menhaden oil* from *Alosa menhaden*, *sardine-* and *herring-oil* from *Clupea sardinus*, *harengus*; *dugong-oil* from the blubber of a large fish (strictly a mammal, *Heliocre dugong*, in Australian and East Indian waters), &c. These are all used for technical purposes only, particularly in the tanning process (except when there is a scarcity of cod-liver oil). Dugong oil has been used as a substitute for cod-liver oil, but in a legitimate way.

The only liver oil in medical use is *cod-liver oil* from *Gadus morrhua.* Up to now it has been supposed to consist, like other fats, chiefly of palmitin, stearin, and oleïn (95 per cent.). Heyerdahl in his researches has proved the fallacy of these suppositions: there is but a small percentage of these acids in the oil, whilst, on the other hand, he has found and determined two hitherto unknown acids, mentioned before—the jecoleïc acid and the remarkable therapic acid.

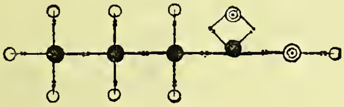
When, through any operation, the alcohol and the acids in the compound ethers are separated the process is called saponification. This may be done by heating the ether with dilute sulphuric acid at a temperature of 110–115°, or with milk of lime at 170° under pressure; or it may be boiled with caustic soda or potash, when sodium or potassium will replace the alcohol, and in the case of glycerides form soaps; those with sodium form hard (toilet) soaps, those with potassium soft soaps. When solutions of soap are treated with sulphuric acid or any other strong acid the alkali is seized by it, forming salts, sulphates, &c., and the fatty acids are set free.

Fats exposed to the influence of air become rancid; a fact only too well known. The chemical nature of this process in all its details are, however, difficult to get at on account of the complex nature of the fats and the great difficulties in recognising and separating compounds so closely allied, both physically and chemically, as the higher homologues of the fatty acids. It is generally represented as a splitting up of the glyceride-molecule through the action of the oxygen of the air, setting glycerin and acids free, afterwards converting the free acids into hydroxy-acids, and by prolonged action splitting both them and the glycerin up, the ultimate products being, as always, carbonic acid and water. Heyerdahl's researches seem, however, to prove that rancidity—in cod-liver oil at any rate—is solely due to introduction of hydroxyls into the glycerides, and not to formation of free acids by splitting up the glyceride-molecule, because he found that by keeping the oil heated for hours at high temperatures (200-300°), while conducting a current of air through it, the rancidity of the oil increased enormously, the acid value at the same time increasing but little (from 0·72–0·77).

As it may often be of importance to ascertain with exactitude how rancid a fat is, or, in other words, how many molecules in a fat have added hydroxyls to themselves (i.e. the proportion of hydroxy-acids in a fat), a process has of late years been devised for this purpose: it is based upon the behaviour of acetic acid towards hydroxy-acids in driving the hydroxyls out and taking their place in the compound as acetyls.

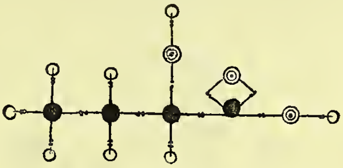
Suppose we have two molecules, one of butyric acid and the other of hydroxy-butyric acid.

FIG. 885



Butyric acid, $C_4H_8O_2$

FIG. 886



Hydroxy-butyric acid, $C_4H_8O_3$

If one hydrogen-atom weighs 1, an atom of carbon weighs 12, and an atom of oxygen 16 (*vide* p. 3) as a consequence:

One molecule of butyric acid weighs:

$$\begin{aligned} C_4 &= 4 \times 12 = 48 \\ H_8 &= 8 \times 1 = 8 \\ O_2 &= 2 \times 16 = 32 \\ &\overline{\quad 88} \end{aligned}$$

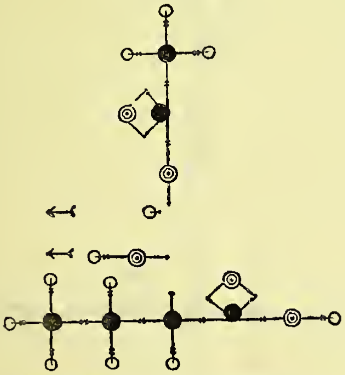
One molecule of hydroxy-butyric acid weighs

$$\begin{aligned} C_4 &= 4 \times 12 = 48 \\ H_8 &= 8 \times 1 = 8 \\ O_3 &= 3 \times 16 = 48 \\ &\overline{\quad 104} \end{aligned}$$

The two molecules together weigh 192.

Now if we let acetic acid act upon the two molecules it will not affect the butyric acid, but will join the other on account of its alcoholic hydroxyl, forming a compound ether-acid on separating a molecule of water.

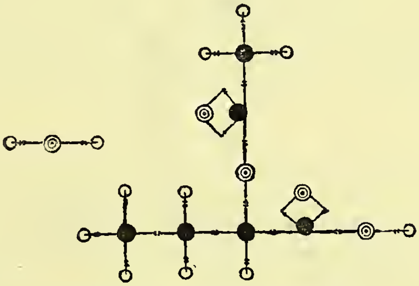
FIG. 887



Acetic acid + hydroxy-butyric acid

=

FIG. 888



Acetyl-hydroxy-butyric acid, $C_6H_{10}O_4$

The weight of the two molecules after acetylisation is therefore:

One molecule of butyric acid—

$$\begin{aligned} C_4 &= 4 \times 12 = 48 \\ H_8 &= 8 \times 1 = 8 \\ O_2 &= 2 \times 16 = 32 \\ & \overline{\phantom{00}88} \end{aligned}$$

One molecule of acetyl-hydroxy-butyric acid—

$$\begin{aligned} C_6 &= 6 \times 12 = 72 \\ H_{10} &= 10 \times 1 = 10 \\ O_4 &= 4 \times 16 = 64 \\ & \overline{\phantom{0}146} \end{aligned}$$

and their aggregate weight $(88 + 146) = 234$.

When we add, without application of heat, potassium-hydrate (KOH) to these acids, potassium will replace hydrogen in each carboxyl.

Fig. 889

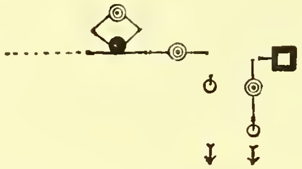
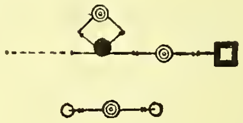


Fig. 890



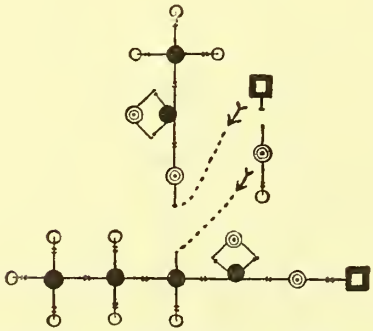
Carboxyl and potassium hydrate = Potassium salt and water

and as there are two carboxyls in the original two molecules as well as in the acetylated molecules, two molecules of KOH are in both cases required to neutralise the acids.

One atom of potassium weighs 39·1; consequently a molecule of potassium-hydrate (KOH) weighs $(39{\cdot}1 + 16 + 1) = 56{\cdot}1$, two molecules 112·2, and three molecules 168·3.

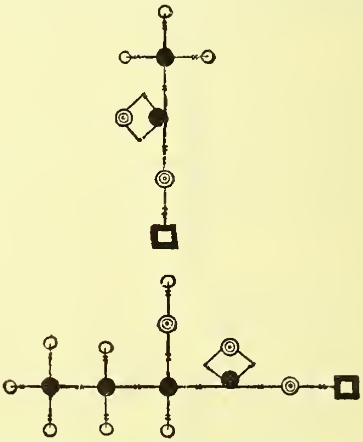
If we *boil* the acids with more KOH, the original acid will remain unaltered, but in the acetylated acid a third potassium-atom will split off the acetyl, forming potassium-acetate, and the original hydroxyl will be restored to the acid:

Fig. 891



Potassium-acetyl-hydroxy-butyrate + potassium hydrate

Fig. 892



Potassium-acetate and potassium-hydroxy-butyrate

We are now able to explain how these processes are utilised in the examination of oils or fatty acids.

We have seen that by the action of cold KOH two atoms of potassium will neutralise the two molecules of the original acids, and that the two molecules of acetylated acids will require the same quantity.

Suppose, therefore, we had 192 milligrammes of the original acids, we should find 112·2 milligrammes of KOH were required to accurately neutralise them. This quantity reduced to 1,000 milligrammes = 1 gramme of the *original* acids ($\frac{112 \cdot 2 \times 1000}{192}$) would make 584·4, which figure is termed acid-value.

We saw that 192 milligrammes of the original acids when acetylated would weigh 234 milligrammes. When treated with cold KOH these acetylated acids would require the same quantity (112·2 milligrammes) of KOH as the original acids for neutralisation, which, if reduced to 1,000 milligrammes of the *acetylated* acids ($\frac{112 \cdot 2 \times 1000}{234}$) would make 479·5 milligrammes, which figure is termed acetyl-acid-value.

If we now boil these neutralised acids with more KOH, the original acids will not be acted upon, as already mentioned, but in the acetylated acids further 56·1 milligrammes of KOH will be used in splitting off the acetyl. This quantity reduced to 1,000 milligrammes of the *acetylated* acids ($\frac{56 \cdot 1 \times 1000}{234}$) makes 239·7 milligrammes, which figure is called acetyl-value.

If we do not first neutralise the acids, but at once boil them with KOH, we shall of course find that the original acids require, as before, 112·2 milligrammes (two molecules) for saturation, which, reduced to 1,000 milligrammes of the *original* acids ($\frac{112 \cdot 2 \times 1000}{192}$), makes 584·4, and is termed saponification-value, which in this case is identical to acid-value.

But if we boil the acetylated acids, before neutralisation in the cold, with KOH, we find that 168·3 milligrammes are required (three molecules, two for neutralisation and one for splitting off the acetyl); reduced to 1,000 milligrammes of the *acetylated* acids ($\frac{168 \cdot 3 \times 1000}{234} = 719 \cdot 2$), the figure 719·2 is termed acetyl-saponification-value.

It will thus be seen that acetyl-value is the difference between acetyl-acid- and acetyl-saponification-values, and the latter is the sum of acetyl-acid- and acetyl-values; therefore, when acetyl-acid- and acetyl-saponification-values agree, and acetyl-value is consequently = 0, no hydroxy-acids can have been present in the compound examined.

By simple calculation we find that if a cod-liver oil has acetyl-value 2, then it contains about 0·15 per cent. of hydroxylated acids, provided the glycerides have about the same molecular weight as therapin or jecoleïn.

Hydroxy-acids not unfrequently show a too low acetyl-value, when they have a hydroxyl in $\gamma$-position, because in that case some of them will form lactones (*vide* p. 182), upon which acetic acid has no effect.

For quantitatively determining the *free fatty acids* in a fat or oil no method has been devised except when the sort of acids present and their relative proportions are known. It is, however, sometimes useful, for the sake of comparison, to know how much potassium-hydrate is required for neutralising such free acids, but it gives no clue to what sort of acid has been neutralised. If, for instance, we say that a certain specimen of cod-liver oil has an acid value of 7·38, and another of 0·34, that does not convey the slightest idea as to the sort of free acids. In such cases it is generally referred to as oleïc acid, although there may not be any free oleïc acid at all present in the fat or oil. The acid-value is therefore only useful for comparing the same sort of fats, in which we may presume there would be present the same acids in the same proportions.

Finally, a method for determining if any unsaturated acids are present in a fat may be mentioned here, although we shall be obliged to treat by anticipation of an element which will have to be subsequently mentioned in its proper place, viz. iodine.

It will be remembered that unsaturated acids—those with double bonds—can add two hydrogens to each double bond, converting them thereby into saturated acids with single bonds (*vide* p. 23). But hydrogens are not the only additions that can be made to the double bonds. The elements of water may be added, as we have seen, one of the valencies taking up the hydroxyl and the other the hydrogen, or two hydroxyls may be added to each double bond. The elements chlorine, bromine, and iodine are also among the additions a double bond will accept. Thus, if we add iodine in excess to an unsaturated acid a certain quantity will be absorbed by the acid and the rest will remain free and unaltered. The quantity of this rest can be determined by analysis, and we then know how much has been absorbed. This absorbed quantity reduced to per cent. of the acid or fat (iodine being absorbed by glycerides as well as by free acids) is termed iodine-absorption.

Taking, for instance, the molecular weight, 282 (grammes, decigrammes, or any other unit of weight), of oleïc acid, and adding 632·5 (i.e. 5 × 126·5, the atomic weight) of iodine, we can illustrate that as one molecule of oleïc acid and five atoms of iodine; iodine we propose to represent by this symbol,

FIG. 893

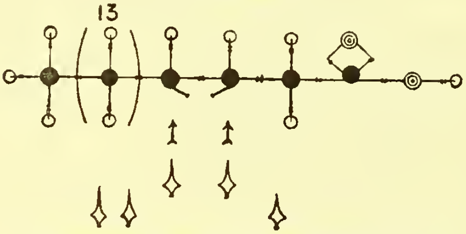
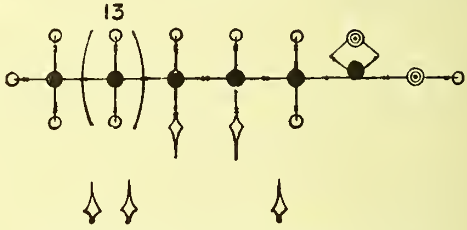


FIG. 894



One molecule of oleïc acid + five atoms of iodine = Di-iodo-oleïc acid + three atoms of iodine

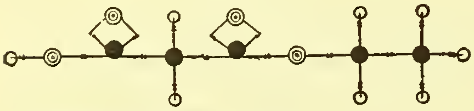
We then learn that out of the 632·5 iodine only 379·5 are to be found as free iodine in the resulting products; consequently 253·0 have disappeared, i.e. have been absorbed by the oleïc acid. These 253·0 calculated as per cent. on the quantity of oleïc acid make $\left(\frac{253 \times 100}{282}\right) = 89 \cdot 7$. Such a figure is termed the iodine absorption of oleïc acid.

This method appears to give good results for oleïc acid, and perhaps for some more of the acids with one double bond; but for oils containing several double bonds, the absorption is so much dependent on the time of action, on the concentration and relative proportions of the solutions employed, on the temperature, and on the solutions being freshly prepared or not, that it is only of value as a comparative agent to be employed under exactly the same circumstances in all cases. But employed with these precautions as a comparative method, it is sometimes possible to draw valuable conclusions as to the constitution of various fats if utilised, as it was by Heyerdahl in his researches on cod-liver oil.

## C. POLYBASIC ACIDS AND ALCOHOLS

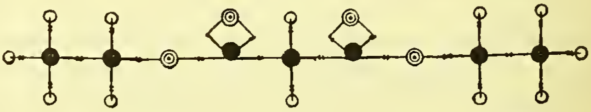
Neutral and acid compounds are formed according as all, or only some, of the acid's carboxyls are joined by alcohols. Malonic acid (fig. 713, p. 184), for instance, forms two ethers, one in which both carboxyls are united to an alcohol, the neutral compound, and another in which only one of the carboxyls is so engaged, the acid compound:

FIG. 895



Ethyl-malonic acid, $C_5H_8O_4$; m.p. 111°·5; acid compound ether

FIG. 896



Malonic ether, ethyl-malonate, $C_7H_{12}O_4$; b.p. 198°; neutral compound ether

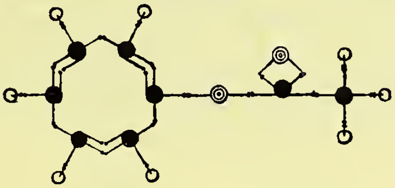
A dibasic acid, also called ethyl-malonic acid, exists, in which ethyl forms a side-chain in malonic acid—consequently not a compound ether, but an isomer to pyrotartaric acid (figs. 719 and 720, p. 185).

Malonic ether has a striking resemblance to aceto-acetic ether (fig. 868, p. 232). They both have a methylene between two carbonyls, and they have therefore the same chemical properties, as explained on p. 228.

## II. Aliphatic Acids and Phenols

Examples of this class are

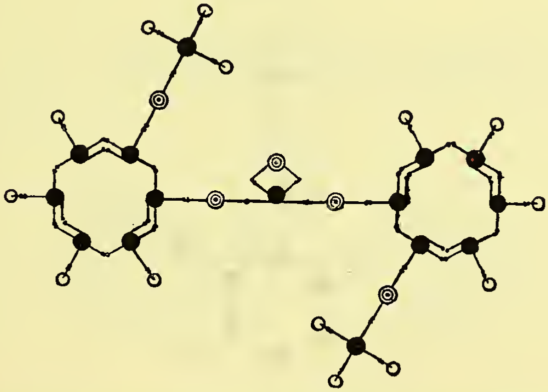
Fig. 897



Phenyl-acetate, $C_8H_8O_2$ ; b.p. 193°

From a phenol-ether, *guaiacol* (fig. 499, p. 118), and a dibasic acid, *carbonic acid*, a neutral compound ether is formed:

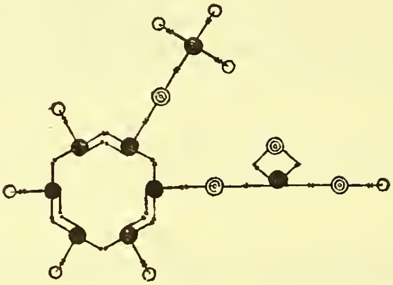
Fig. 898



Guaiacol-carbonate, $C_{15}H_{14}O_5$ ; m.p. 85° ; antiseptic and antipyretic ; used for tuberculosis, especially for phthisis, as a substitute for creasote and for the pure guaiacol, it not affecting the stomach

Also the acid compound is known :

Fig. 899



Guaiacol-carbonic acid, $C_8H_8O_4$ ; m.p. 150° ; antiseptic and antipyretic

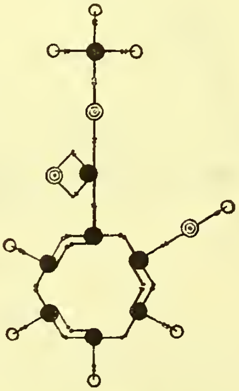
Creosotal is a new remedy prepared from 'sodium-creosote and chloro-carbonic acid' (carbonic acid in which one of the two hydroxyls (p. 273) has been displaced by chlorine). In the case of creasote from wood-tar being employed creosotal will be identical with guaiacol-carbonic acid; creasote from coal-tar would form phenol-carbonic acid of analogous structure (*vide* creasote, p. 119). It is not stated which creasote is to be employed, but probably that from wood-tar is meant.

Similar combinations of guaiacol and creosol (from wood-tar creasote), or phenol and cresol (from coal-tar creasote) with oleïc acid, have been prepared, and are known by the names of oleo-guaiacol and oleo-creasote: substitutes for salol (comp. p. 248).

## III. Cyclo-acids and Alcohols

When *methyl-alcohol* is joined to the carboxyl of *salicylic acid* (fig. 823, p. 215) a compound ether is formed :

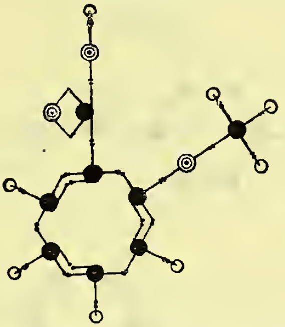
Fig. 900



Methyl-salicylate, $C_8H_8O_3$ ; b.p. 224° ; chief constituent of winter-green- (gaulteria-) oil (90 per cent.) used for articular rheumatism

If *methyl-alcohol* joins the *phenol-hydroxyl* an ether acid (*vide* p. 250) is formed:

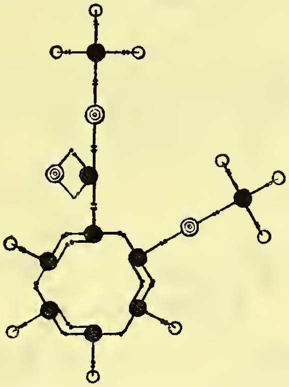
FIG. 901



Methyl-salicylic acid, $C_8H_8O_3$; m.p. 98°·5

and if *methyl-alcohol* joins both the *carboxyl-* and the *phenol-hydroxyl* we have again a compound ether:

FIG. 902

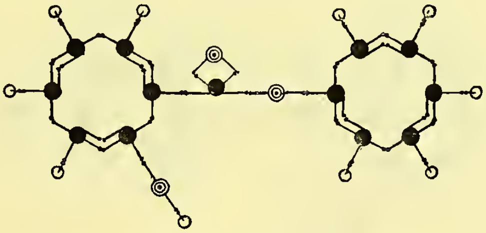


Di-methyl-salicylate, $C_9H_{10}O_3$; b.p. 228°

## IV. Cyclo-acids and Phenols

From *salicylic acid* and *phenol*:

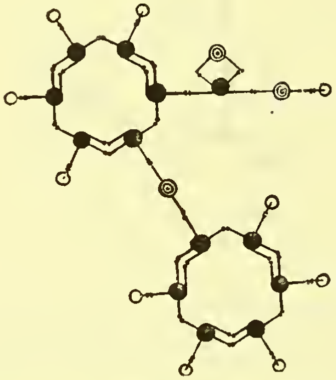
FIG. 903



Salol, phenyl-salicylate, $C_{13}H_{10}O_3$; m.p. 42°; used for acute rheumatism, and externally as an antiseptic and deodorant like iodoform. It has its name, not from salicyl and phenol, which seems a natural conclusion, but from a Dr. Sahli, who was the first to recommend and report upon it (*Heger. neue Arzneim*)

When its sodium salt is heated to 300° the phenyl jumps over to the phenol-hydroxyl (intramolecular change, *vide* p. 40) and forms an ether-acid (*vide* p. 250).

Fig. 904

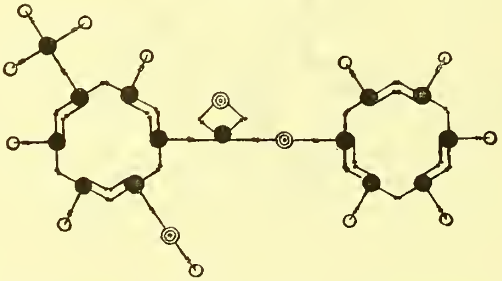


Phenyl-salicylic acid, $C_{13}H_{10}O_3$ (*Ber.* xxi. p. 501)

Salacetol, m.p. 71°, is a compound in which acetone, instead of phenyl, is joined to salicylic acid in salol: recommended as an improvement upon salol.

From *para-cresotic acid* (fig. 838, p. 223) and *phenol* we obtain

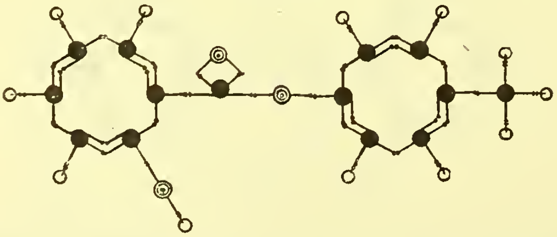
Fig. 905



Methyl-salol, phenyl-para-cresotate, $C_{14}H_{12}O_3$; m.p. 92°; antirheumatic, analogous to salol

From *salicylic acid* and *para-cresol* (fig. 430, p. 95):

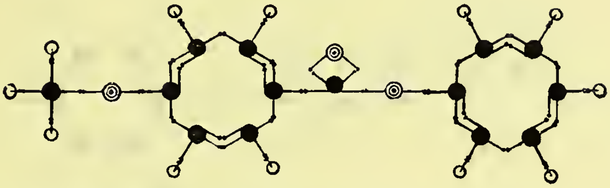
Fig. 906



Cresalol, para-cresol-salicylate, $C_{14}H_{12}O_3$; m.p. 39°; used as substitute for salol

From *anisic acid* (an ether-acid, fig. 918, p. 251) and *phenol*:

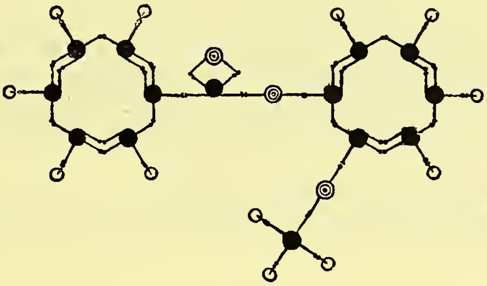
FIG. 907



Phenyl-anisate, $C_{14}H_{12}O_3$; m.p. (?); antirheumatic, analogous to salol

From *benzoic acid* and *guaiacol*:

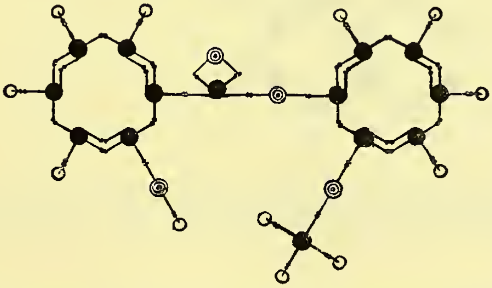
FIG. 908



Benzosol, guaiacol-benzoate, benzoyl-guaiacol, $C_{14}H_{12}O_3$; m.p. 50°; used in phthisis

From *salicylic acid* and *guaiacol*:

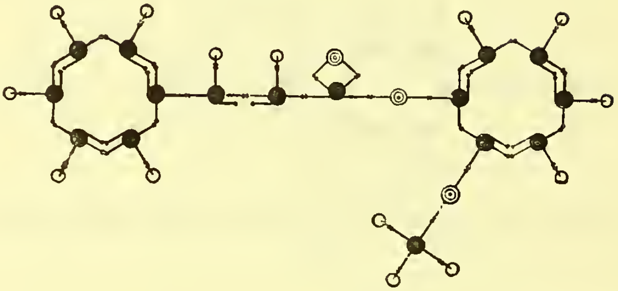
FIG. 909



Guaiacol-salicylate, $C_{14}H_{12}O_4$; analogous to the other guaiacol-compounds

From *cinnamic acid* (fig. 821, p. 214) and *guaiacol*:

Fig. 910



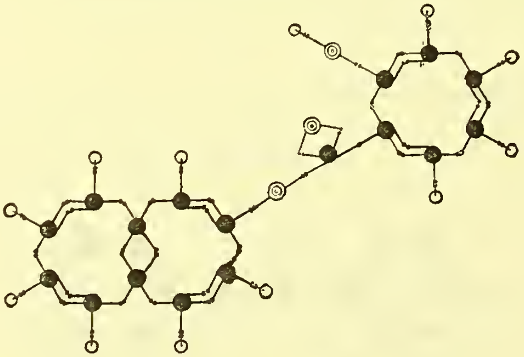
Styracol, cinnamyl-guaiacol, $C_{16}H_{14}O_3$; m.p. 130°; is recommended as a powerful antiseptic, internally for phthisis, blennorrhœa, and gonorrhœa, and as an intestinal antiseptic; externally it acts like iodoform.

The object of all these synthetical compounds of guaiacol is to avoid the injurious effects of the pure drug upon the mucous membrane of the stomach. They all pass unaltered, or almost so, through the stomach, because of the acidity of its contents; but when they reach the small intestines and are mixed with the alkaline pancreatic juice, they break up into their components (saponification). Besides, the pure guaiacol has a loathsome taste, which is entirely disguised in these compounds.

We know also compound ethers formed from naphthol.

Thus from *β-naphthol* and *salicylic acid* (fig. 452, p. 103, and fig. 823, p. 215):

Fig. 911

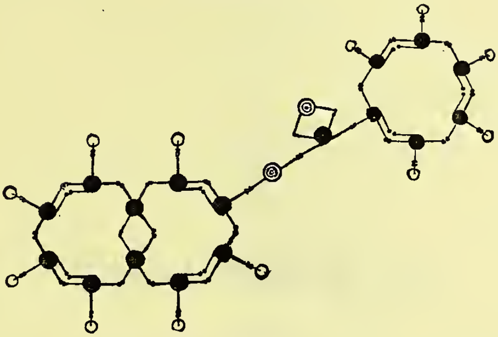


Betol, naphthol salicylate, naphthalol, naphthol-salol, sali-naphthol, $C_{17}H_{12}O_3$; m.p. 95°; used for the same purposes as salol, but preferred by many in gonorrhœic cystitis and articular rheumatism; tasteless and odourless

Alphol is the *a*-combination.

The same *naphthol* forms with *benzoic acid* a similar compound:

Fig. 912



Benzo-naphthol, β-naphthol-benzoate, $C_{17}H_{12}O_2$ ; m.p. (?); intestinal antiseptic; splits up in the body into β-naphthol, which passes into the intestines, and benzoic acid, which is carried away through the bladder partly as hippuric acid

## F. ETHER-ACIDS

If we join an alcohol to the alkyl-part of a *fundamental* aliphatic acid, we do not form a compound which has not been already mentioned; we simply obtain a higher homologue of the acid. Take, for instance, *methyl-alcohol* and join it in the way mentioned to *acetic acid*, and propionic acid is formed.

Fig. 913

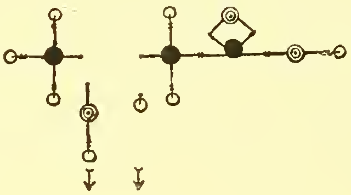


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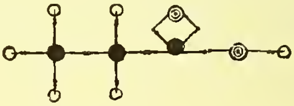
Fig. 914



Methyl-alcohol + acetic acid = Propionic acid (fig. 669, p. 176)

The result is different if we perform the operation on a *hydroxy-acid*, having an alcoholic hydroxyl which can form an ether with another alcoholic hydroxyl.

The process is in every respect analogous to ether-formation, p. 113, and the resulting compounds are therefore termed ether-acids.

The aliphatic compounds are not very important, and it will be sufficient to illustrate a typical example:

Fig. 915

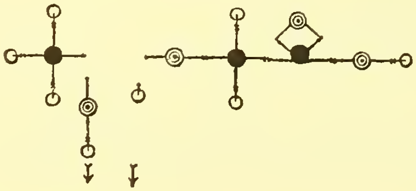


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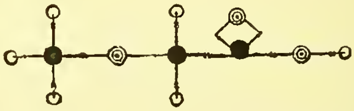
Fig. 916

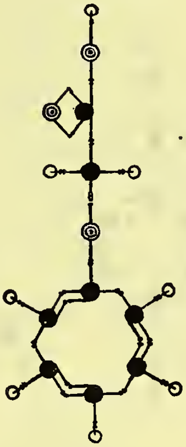


Methyl-alcohol + glycollic acid (fig. 691, p. 179) = Methyl-glycollic acid, methoxy-acetic or oxy-methyl-acetic acid (comp. p. 81), $C_3H_6O_3$ ; b.p. 206°

More important are the combinations of hydroxy-acids with phenols, phenol-ethers, &c., or hydroxy-cyclo-acids with alcohols.

From *glycollic acid* and *phenol*:

Fig. 917

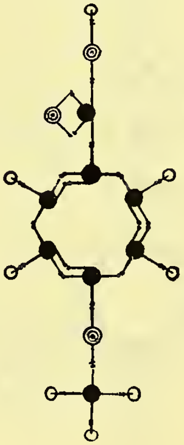


Phenol-glycollic acid, phenyl-oxy-acetic acid, $C_8H_8O_3$; m.p. 96°; powerful antiseptic

We have had another combination of the two compounds, an aromatic acid, mandelic acid (fig. 816, p. 213, where phenol was substituting a hydrogen of glycollic acid), possessing, it seems, no therapeutic properties.

From *para-hydroxy-benzoic acid* (p. 216) and *methyl alcohol*, also derivable from *anisic aldehyde* (fig. 560, p. 136):

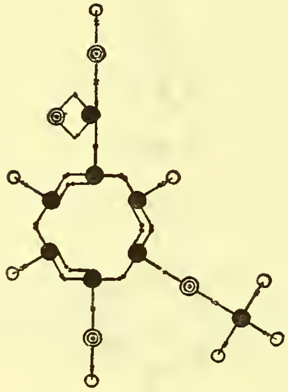
Fig. 918



Anisic acid, para-methoxy-benzoic acid, $C_8H_8O_3$; m.p. 184°; used mostly as sodium salt, instead of sodium salicylate, as an antiseptic

From *protocatechuic acid* (fig. 828, p. 219) and *methyl-alcohol*, or from oxidation of *vanillin* (fig. 562, p. 136), is derived

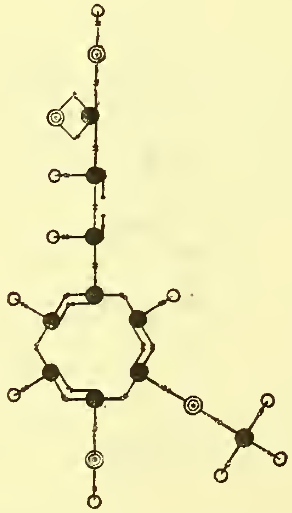
Fig. 919



Vanillic acid, $C_8H_8O_4$; meta-methyl-ether-protocatechuic acid; m.p. 207°

From *caffeïc acid* (p. 220) and *methyl-alcohol*, or from *coniferyl-alcohol* (fig. 511, p. 123), by oxidation:

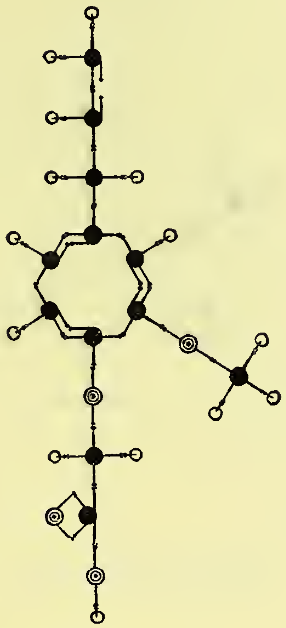
Fig. 920



Ferulic acid, $C_{10}H_{10}O_4$; m.p. 168°; occurs in asafœtida

From *glycollic acid* and *eugenol*:

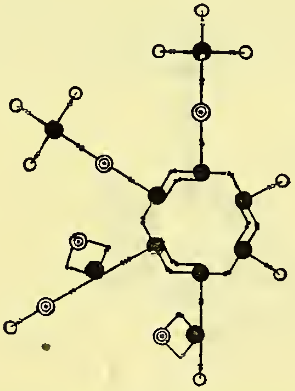
FIG. 921



Eugenol-acetic acid, $C_{12}H_{14}O_4$

An ether-acid containing an aldehyde may also be placed in this class, viz. opianic acid: its structure will be seen from the illustration:

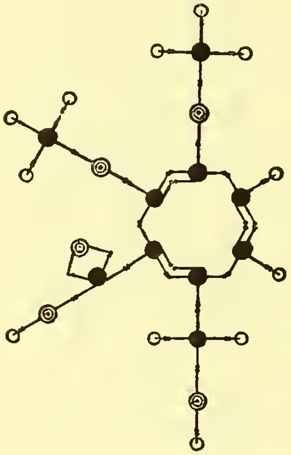
FIG. 922



Opianic acid, $C_{10}H_{10}O_5$; m.p. 145°; as an anhydride it is a constituent of hydrastine and narcotine

Another ether-acid, containing, however, an alcohol instead of the aldehyde in opianic acid is

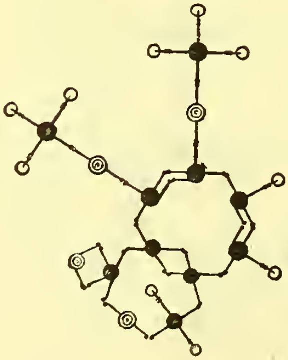
Fig. 923



Meconinic acid, $C_{10}H_{12}O_5$

Only alkyl-derivatives are known; the acid itself, as soon as it is isolated, forms an anhydride or lactone, meconine.

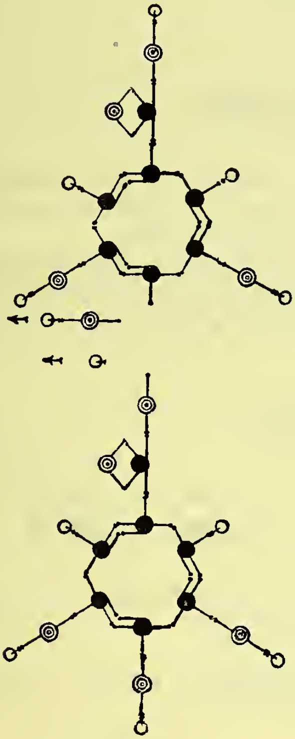
Fig. 924



Meconine, $C_{10}H_{10}O_4$; m.p. 102°; one of the constituents of opium

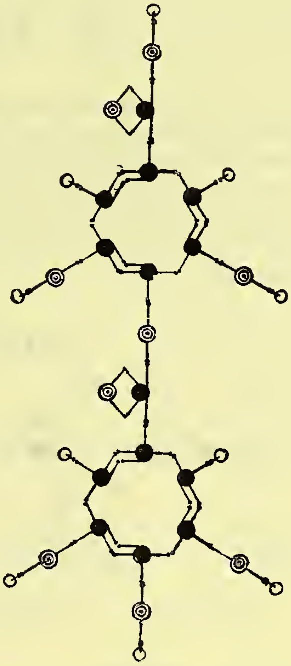
We have seen (fig. 859, p. 229) one way in which two molecules of gallic acid can join each other. Another way of combination is to join the carboxyl of one molecule to an alcoholic hydroxyl of another molecule, forming an ether acid :

Fig. 925



Two molecules of gallic acid

Fig. 926



Tannin, gallo-tannic acid, $C_{14}H_{10}O_9$

Chief constituent of nutgalls ; present also in tea

We have already had occasion to mention some other ether-acids, viz. methyl-salicylic acid (fig. 901, p. 245) and phenyl-salicylic acid (fig. 904, p. 246). Another, lacto-lactic acid (fig. 933, p. 257), has a formation analogous to gallo-tannic acid above.

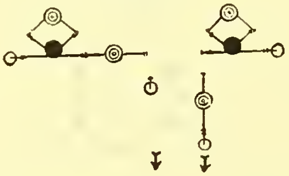
## G. ACID-ANHYDRIDES

We have previously referred to one sort of anhydrides, the lactones (p. 182), formed from *one* molecule of acid, whereas the real acid-anhydrides are formed from *two* molecules, in both cases one molecule of water being abstracted from their carboxyl-parts (hence the name).

Most of the acids are capable of forming anhydrides, and the process is analogous to the formation of ethers (p. 113). As with them, so the acids can form simple anhydrides when the two molecules are of the same sort, or mixed anhydrides, when the two molecules are of different acids. A few examples will suffice.

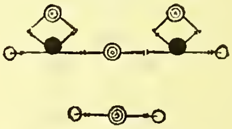
### SIMPLE ANHYDRIDES

Fig. 927



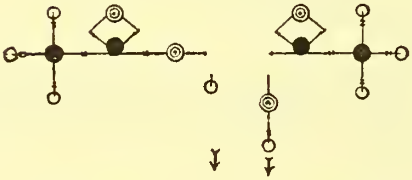
Formic acid + formic acid

Fig. 928



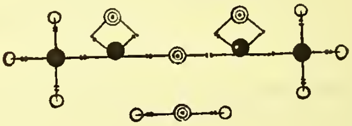
Formic anhydride, $C_2H_2O_3$, is not prepared

Fig. 929



Acetic acid + acetic acid

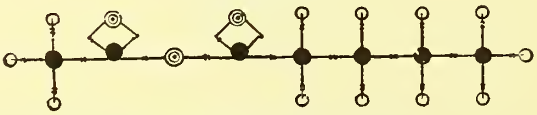
Fig. 930



Acetic anhydride, $C_4H_6O_3$; b.p. 138°

### MIXED ANHYDRIDES

Fig. 931



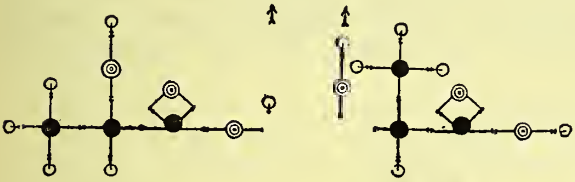
Acetic-valeric-anhydride, $C_7H_{12}O_3$

Hydroxy-acids with a hydroxyl in $\alpha$-position (as to $\beta$- and $\gamma$-positions *vide* p. 182) behave differently, and sometimes more complicate matters, on account of their alcoholic hydroxyl, which they seem to let go, rather than part with their carboxyl-hydroxyl. Consequently we find that the anhydrides of these acids are not formed as above by two carboxyl-ends joining (dropping a molecule of water), but by the joining of the carboxyl-end of one of the molecules to the alcoholic hydroxyl in the other (with elimination of *one* molecule of water), in which case the product is monobasic ether-acid, as it has still one carboxyl unaltered (*vide* fig. 933, below). Or, real anhydrides are formed, when each of the two carboxyls joins an alcoholic hydroxyl of the other molecule, with separation of *two* molecules of water (*vide* fig. 935, below). There is still a third mode of combining the two molecules by joining the two alcoholic hydroxyls, when a dibasic ether-acid results on account of the two carboxyls left undisturbed.

These three combinations will be easily understood from the illustrations:

1. The carboxyl of one molecule joining the alcoholic carbon of another:

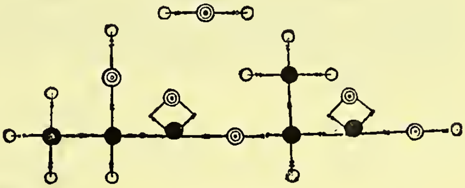
Fig. 932



$\alpha$-Lactic acid (*vide* fig. 692, p. 179)

+ $\alpha$-Lactic acid. The arrangement of the links has been altered, according to what is stated on p. 8, in order to make the two links join more comfortably

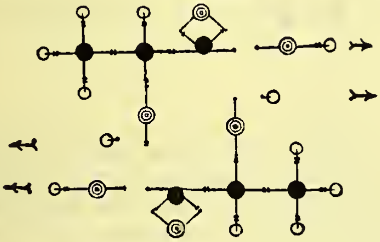
Fig. 933



Lactolactic acid, $C_6H_{10}O_5$; decomposes on heating; usually called lactic anhydride, though a monobasic acid

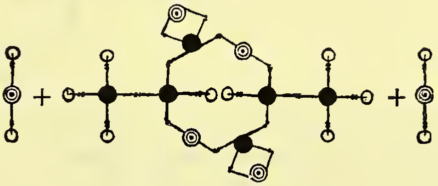
2. Carboxyl and alcoholic carbon of one molecule joining the alcoholic carbon and carboxyl of another:

Fig. 934



Two molecules of $\alpha$-lactic acid

Fig. 935



Lactide, $C_6H_8O_4$; m.p. 125°

Comp. p. 183, where another interpretation is represented.

3. The alcoholic carbon of one molecule joining the alcoholic hydroxyl of another:

Fig. 936

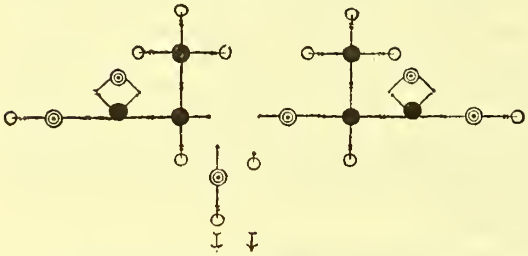
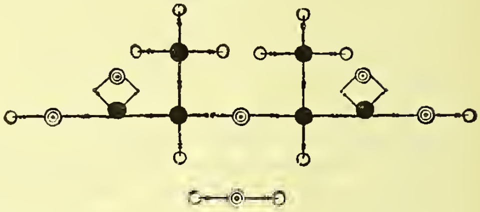


Fig. 937

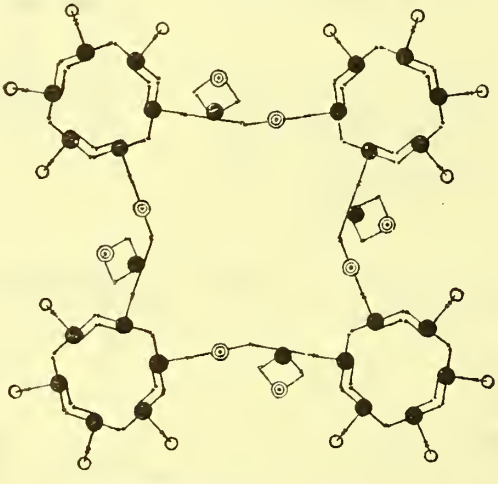


Two molecules of α-lactic acid joining with their alcoholic hydroxyls = Di-lactic acid, $C_6H_{10}O_5$; di-basic acid; decomposes on heating

Anhydrides are neutral compounds, therefore the first and the last of the above compounds are not strictly belonging to this class of bodies, as they are, one a mono-, the other a di-basic ether-acid.

'Lactide' was, up till quite recently, the only *lactide* more closely examined. Glycolide (*vide* p. 182) is probably formed, not from one molecule of glycollic acid, but from several. Other lactides have been formed from aromatic acids, some from one molecule, others from several molecules, of the acid by separation of a corresponding number of molecules of water. A lactide of salicylic acid, poly-salicylide, has been prepared (*Ber.* xxv. p. 3501), its structure being represented thus:

Fig. 938



Salicylide, $C_{28}H_{16}O_8$; m.p. 261°

Similar compounds from the homosalicylic (cresotic) acids (p. 223) have been prepared. They are said to be of considerable importance, as they combine with chloroform, producing well-formed crystals, in which chloroform plays the same part as water does in other crystallised compounds, one molecule of salicylide combining with two molecules of chloroform. This salicylide-chloroform contains the chloroform, of course free from all impurities, and may be kept any length of time in closed vessels perfectly unaltered. In the air, and by heating, the chloroform is given off, and can thus be obtained pure, and the remaining salicylide may be used over and over again for the same purpose. The *o*-homo-salicylide-chloroform keeps better than any of the others (*Ber.* xxv. p. 3512).

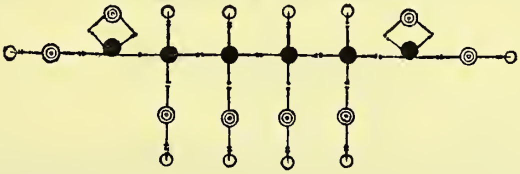
# OXYGEN-SUBSTITUTIONS IN CLOSED CHAINS

We have already been acquainted with some cyclo-compounds in which one or more carbon-atoms forming links in the ring itself may be considered substituted by an oxygen-atom. Thus we have had di-ethylene oxide (fig. 489, p. 115), paraformic aldehyde (fig. 537, p. 131), and paraldehyde (fig. 540, p. 131) as instances of hexagonal rings; æsculetin (fig. 836, p. 222) as an interlocked hexagon; succinic anhydride (fig. 716, p. 185) and lactones (fig. 701, p. 182) as pentagons; safrol (fig. 505, p. 120), apiol (fig. 506, p. 121), piperonal (fig. 564, p. 137), as interlocked pentagons.

There are still some more, the derivation of which is interesting.

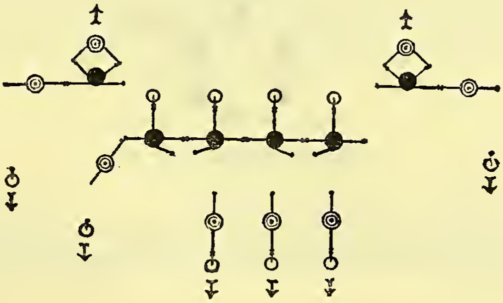
One of these is furane or furfurane, derived from *mucic acid* (fig. 733, p. 188), whose structure is this (placing, however, all the alcoholic hydroxyls in one line in order to make the process plainer):

Fig. 939



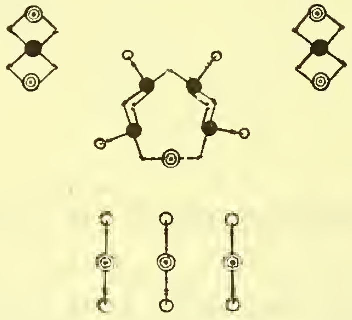
We then proceed to remove the two carboxyls and as many hydroxyls as will form water:

Fig. 940



The part of the chain left unbroken now bends to unite the free valencies at each end, the detached atoms forming carbon-dioxide and water:

Fig. 941

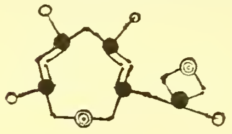


Furfurane, $C_4H_4O$; b.p. 32°

Cross-bindings between the carbon-atoms instead of double bonds, analogous to diagonal bonds in benzene (fig. 284, p. 54), have also been suggested.

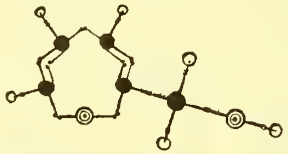
This pentagonal ring forms, exactly like benzene, combinations with alcohols, aldehydes, acids, &c.

Fig. 942



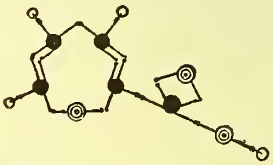
Furfurol, furfurane-aldehyde, $C_5H_4O_2$; b.p. 161°·5

Fig. 943



Furfur-alcohol, $C_5H_6O_2$; varnish-like when dried

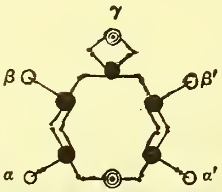
Fig. 944



Pyro-mucic acid, $C_5H_4O_3$; m.p. 134°·5

A hexagonal ring also having a carbon-atom substituted by oxygen, is γ-pyrone, which may be looked upon as formed in a similar way from a hydroxylated acetone-di-acetic acid.

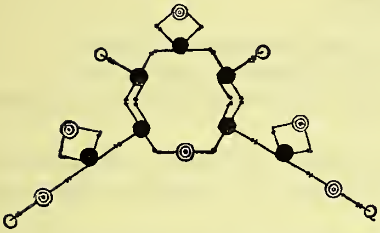
Fig. 945



γ-Pyrone, $C_5H_4O_2$; m.p. 32°

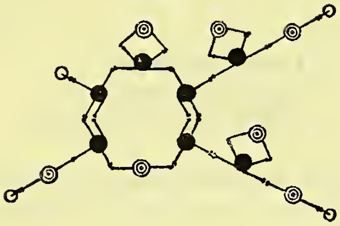
Besides γ-pyrone, an α-pyrone with carbonyl in α-position is also known, m.p. 207°. Several compounds are derivable from these rings; thus the γ-pyrone combines with carboxyls and also with hydroxyls, forming acids:

Fig. 946



Chelidonic acid, $C_7H_4O_6$; m.p. 262°; occurs in *Chelidonium majus*

Fig. 947



Meconic acid, $C_7H_4O_7$; crystals; decomposes on heating; the exact positions of the carboxyls and hydroxyl are not known; occurs in opium

## Future Nomenclature of the Mutual Combinations of Oxygen-compounds

There are but two of these classes specially mentioned in the Congress rules, viz. compound ethers and acid-anhydrides, both retaining the present mode of forming their names, of course with the alterations necessitated by the preceding rules. The nomenclature of the other classes may be regulated by the rules already stated.

Examples are—

### Aldehyde and Ketone Acids

| *Old Nomenclature* | | | *New Nomenclature* |
|---|---|---|---|
| Formyl-acetic acid | | (fig. 849, p. 227) = | Propanaloïc acid |
| Pyro-racemic acid | | (fig. 851, p. 227) = | Propanonoïc acid |
| Aceto-acetic acid | ketone form | (fig. 853, p. 227) = | Butan-2 onoïc acid |
| | alcoholic form | (fig. 857, p. 228) = | 2 Buten-2 oloïc acid |
| Levulinic acid | | (fig. 855, p. 228) = | Pentan-2 onoïc acid |

### Compound Ethers

| | | |
|---|---|---|
| Methyl-formate | (fig. 861, p. 231) = | Methyl-methanoate |
| Methyl-acetate | (fig. 863, p. 231) = | Methyl-ethanoate |
| Aceto-acetylic ethyl ether | (fig. 868, p. 232) = | Ethyl-butan-2 onoate |
| Triacetin | (fig. 875, p. 234) = | Propyl-triethanoate |
| Ethyl-malonic acid | (fig. 895, p. 242) = | Ethyl-propanedioïc acid[1] |
| Malonic ether | (fig. 896, p. 242) = | Ethyl-propanedioate |

Both the German and French commentators use methyl, ethyl, &c., in their examples, though they cannot be considered side-chains in the compounds, and though they are termed methane, ethane, &c., in the analogous ethers (methane-oxy-methane). If the latter designation were employed it would serve as a more ready means of distinguishing compound ethers from the isomeric dibasic acids.

### Ether acids

| | | |
|---|---|---|
| Methyl-glycollic acid | (fig. 916, p. 250) = | Methane-oxy-ethanoïc acid (?) |

---

[1] The dibasic ethyl-malonic acid (*vide* p. 243) would in nomenclature be distinguishable from the compound ether by the numeral only: 2 ethyl-propanedioïc acid.

## Acid-anhydrides

Formic anhydride (fig. 928, p. 256) = Methanoïc anhydride
Acetic anhydride (fig. 930, p. 256) = Ethanoïc anhydride
Acetic-valeric anhydride (fig. 931, p. 256) = Pentanoïc ethanoïc anhydride

There is no rule to guide us in forming the name of lactide and similar compounds indicating the formation of a hexagon by the elimination of two molecules of water from two molecules of acid.

Nothing shows better than paragraph 30 of the Congress Resolutions that the French Committee have been thinking of their own *conventions* only; the paragraph runs thus:—

'*On conserve les conventions actuelles pour les sels et les éthers composés.*'

Now it happens, as we know, that German chemists distinguish the latter bodies as esters, and they, of course, construe the resolution as referring to their mode of designation. Therefore we find ethyl-succinate termed *Butandisäure æthylester* in the German *exposé* of the Congress rules (*Ber.* xxvi. p. 1614) and *butanedioate d'éthyle* in the French (*Agenda du Chimiste*, 1893, p. 484). A complete conformity of nomenclature in the different languages is in this way impossible.

# PART VIII.

# Halogen Compounds

# Chlorine-, Bromine-, and Iodine-compounds

*Index*, ◇ *Chemical Symbols*, Cl, Br, I.

We have now to call upon other elements in order to form new compounds. Amongst them the three allied elements, chlorine, bromine, and iodine, collectively termed *halogens*, are prominent (*fluorine* compounds being of minor interest). They are elements like hydrogen, which they can replace in nearly every instance where it occurs in a compound, and, also like hydrogen, add themselves to compounds in which there are double or triple bindings.

As index of a halogen in our pictorial representations is used the figure ◇; the text will indicate which of the three halogens is thus represented.

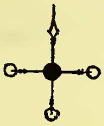
From the enormous number of halogen-substituted compounds only those will be discussed which have been introduced into materia medica, or may have a bearing upon them.

## HALOGEN-DERIVATIVES FROM HYDROCARBON

### Methane-derivatives

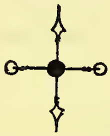
One after the other, the hydrogen-atoms in methane may be replaced by a halogen:

Fig. 948



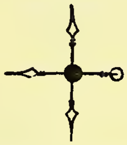
Mono-chloro-methane, methyl-chloride, $CH_3Cl$; a gas; b.p. – 23°

Fig. 949



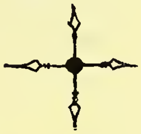
Methylene chloride, $CH_2Cl_2$; b.p. 41°·6

Fig. 950



Chloroform, $CHCl_3$; b.p. 61°·2

Fig. 951



Tetra-chloro-methane, $CCl_4$; b.p. 76°·6

Methyl-chloride is used as an artificial cold-producer; also as a local anæsthetic spray for ischias and neuralgia. A saturated solution of methyl-chloride in chloroform is known by the name of compound liquid.

Methyl-bromide, *brommethyl*, $CH_3Br$, is a gas, b.p. 4°·5.

Methyl-iodide, $CH_3I$, a liquid, b.p. 42°·5, is prepared on a large scale in the manufacture of dyes.

Methylene-chloride is used as an anæsthetic instead of chloroform.

Methylene-bromide, $CH_2Br_2$, b.p. 82°.

Methylene-iodide, $CH_2I_2$, m.p. 4°, b.p. 180°, is a poison when subcutaneously injected, or even inhaled.

Chloroform Pictet is prepared by cooling chloroform to $-80°$, and having removed such impurities as solidify above that temperature, by further lowering the temperature to $-82°$, when the chloroform solidifies and can be separated from those impurities which still remain liquid. Another method of preparing pure chloroform through salicylide has already been mentioned, p. 258.

Bromoform, $CHBr_3$, b.p. 151°, is used as a specific for whooping-cough.

Iodoform, $CHI_3$, m.p. 119°, an extensively used antiseptic, has an unpleasant smell.

Tetra-chloro-methane is a dangerous anæsthetic.

Tetra-bromo-methane, $CBr_4$, m.p. 92°·5.

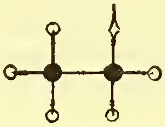
Tetra-iodo-methane, $CI_4$, decomposes on heating.

## Ethane-derivatives

The formation of different compounds from ethane depends, not only on the number of halogen atoms, but also on the way in which they are distributed between the two carbon-atoms; therefore there are two series of halogen-derivatives of the di-, tri-, and tetra-substitution-products, while mono-, penta-, and hexa-halogen-derivatives are common to both.

Common to both series:

Fig. 952

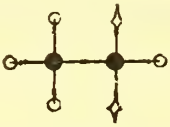


Ethyl-chloride, $C_2H_5Cl$; b.p. 12°·5

Ethylidene-series, *asymmetrical*, in which the halogens are placed as *near* one another as possible. No distinction between the various positions on the same carbon-atom.

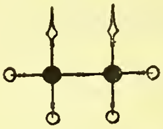
Ethylene-series, *symmetrical*, in which the halogens are placed as *far* from one another as possible, without distinguishing the different positions on the same carbon-atom.

Fig. 953



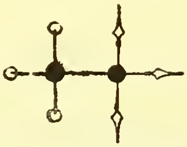
Ethylidene-chloride, $C_2H_4Cl_2$; b.p. 58°

Fig. 954



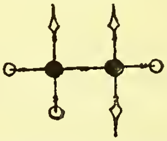
Ethylene-chloride, $C_2H_4Cl_2$; b.p. 85°

Fig. 955



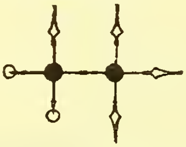
Mono-chlor-ethylidene-chloride, $C_2H_3Cl_3$; b.p. 74°

Fig. 956



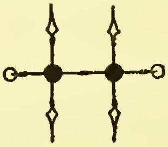
Mono-chlor-ethylene-chloride, $C_2H_3Cl_3$; b.p. 115°

Fig. 957



Di-chlor-ethylidene-chloride, $C_2H_2Cl_4$; b.p. 135°

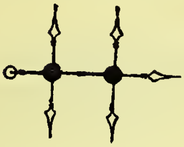
Fig. 958



Di-chlor-ethylene-chloride, $C_2H_2Cl_4$; b.p. 147°

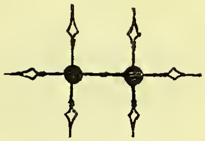
Common to both series:

Fig. 959



Penta-chlor-ethane, $C_2HCl_5$; b.p. 159°

Fig. 960



Per-chlor-ethane, $C_2Cl_6$; m.p. and b.p. 185°

Ethyl-chloride, *chlor-ethyl*, *chelen* or *kelen*, $C_2H_5Cl$ (fig. 952), has lately been recommended as an anæsthetic instead of methyl-chloride (*Ph. Ztg.* 1891, p. 569). Chloryl is a mixture of methyl- and ethyl-chloride.

Ethyl-bromide, *bromethyl*, *hydrobromic ether*, *ether bromatus* (fig. 952), $C_2H_5Br$, b.p. 38°. Anæsthetic for minor (dental &c.) operations; must not be confounded with brom-methyl (fig. 948), still less with the poisonous ethylene bromide (fig. 954).

Ethyl iodide, $C_2H_5I$, b.p. 72°·5 (fig. 952). Used for inhalation in cases of asthma; poisonous.

Ethylidene chloride, *ethidene chloride*, $C_2H_4Cl_2$ (fig. 953). Anæsthetic, especially in dental operations; asserted to be less dangerous than chloroform.

Mono-chlor-ethylidene-chloride, *methyl-chloroform*, *trichlor-ethane*, $C_2H_3Cl_3$ (fig. 955). Anæsthetic; is also said to be less dangerous than chloroform, and preferred on that account in cases where a rapid narcosis is not indispensable.

Ethylene-chloride, *ethylene bi-chloride*, *Dutch liquid*, $C_2H_4Cl_2$ (fig. 954). Has been recommended as an anæsthetic in preference to chloroform.

Ethylene-bromide, $C_2H_4Br_2$, b.p. 131° (fig. 954), is poisonous in doses in which ethyl-bromide is usually prescribed. It having recently been recommended as a substitute for potassium bromide in epilepsy, the greatest care should be taken to prevent mistakes.

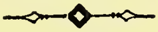
There are one or two more compounds named ethylene-bromides (*vide* fig. 966, p. 268), but fortunately they have not yet found their way into materia medica.

Ethylene-iodide, $C_2H_4I_2$, m.p. 73° (fig. 954), is also poisonous.

Aran's ether anæsthetic, is a mixture of tri-, tetra- and penta-chlor-ethane.

Instead of chlorine, itself, a chloride of a dyad metal may replace a hydrogen-atom of the hydrocarbons. Such a dyad metal is mercury (chemical symbol Hg, illustrating index —◆— see p. 175), which combines with two atoms of chlorine, forming mercuric chloride, commonly called *corrosive sublimate*:

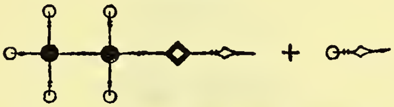
Fig. 961



Mercuric chloride, $HgCl_2$

One of its chlorine atoms joins a hydrogen-atom of ethane, and the rest of the mercuric chloride fills the vacant place:

Fig. 962

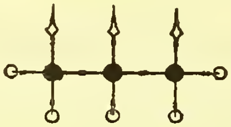


Mercury-ethyl-chloride, $C_2H_5HgCl$; sublimes at 40° without melting; antisyphilitic

## Propane-derivatives

Upwards of seventy different combinations of halogens and propane are known. We shall only mention one or two of them, analogous to glycerin (fig. 375, p. 78) in their structure:

Fig. 963

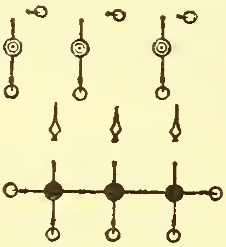


Tri-chloro-propane, tri-chlorhydrin, glyceryl-tri-chloride, $C_3H_5Cl_3$; b.p. 158°

Tri-bromo-propane, *tri-bromhydrin*, *glyceryl-tri-bromide*, *allyl-tri-bromide*, $C_3H_5Br_3$, b.p. 219°. Antispasmodic; a remedy for whooping-cough.

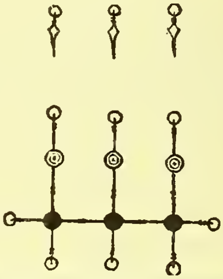
When tri-chloro-propane is heated with water to 160° the three atoms of chlorine are exchanged for hydroxyls, glycerin and hydrochloric acid being formed:

Fig. 964



One molecule of tri-chloro-propane and three molecules of water

Fig. 965

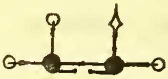


One molecule of glycerin ($C_3H_8O_3$) and three molecules of hydrochloric acid (HCl)

## Ethylene-derivatives

There may be two series of these halogen compounds, analogous to the ethane-derivatives.
Common to both series:

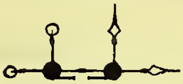
Fig. 966



Chlor-ethylene, *vinyl-chloride*, $C_2H_3Cl$; a gas; b.p. −18°.
Brom-ethylene, *vinyl-bromide*, $C_2H_3Br$; b.p. 16°.
Iod-ethylene, *vinyl iodide*, $C_2H_3Br$; b.p. 56°.

Asymmetrical Series

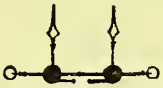
Fig. 967



Asymmetrical di-chlor-ethylene, $C_2H_2Cl_2$; b.p. 37°

Symmetrical Series

Fig. 968



Symmetrical di-chlor-ethylene, acetylene di-chloride, $C_2H_2Cl_2$; b.p. 55°

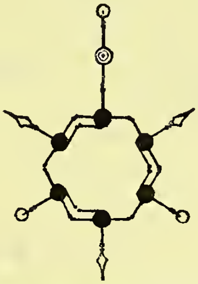
and so forth.

## Alcohol- and Phenol-derivatives

Halogens will replace the hydrogen-atom in an alcohol's radical, but not the hydrogen of the hydroxyl. The hydroxyl itself may, however, be replaced, whereby halogen-derivatives of the hydrocarbons are arrived at.

The same rule seems to be general as regards the phenols. In them the hydrogen-atoms belonging to the ring may easily be substituted by halogens. Thus we have

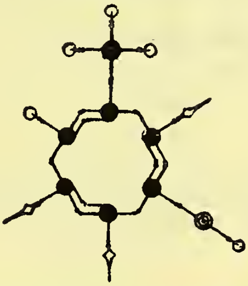
Fig. 969



s-Trichloro-phenol, $C_6H_3Cl_3O$; m.p. 67°; a powerful antiseptic, said to be twenty-five times as powerful as carbolic acid; its calcium salt is also used

Tribromo-phenol, *bromol*, $C_6H_3Br_3O$, m.p. 92°–95°, is also a strong antiseptic. It has been administered both externally in tuberculous processes, gangrene, diphtheria, &c., and internally as a disinfectant of the bowels, as it remains undissolved by the gastric juice, and has, particularly as bismuth-phenolate, given the best results of all antiparasitic remedies in cholera cases (Hueppe, 'Die Choleraepidemie in Hamburg, 1892,' *Berlin. klin. Wochenschrift*, February 1893, p. 162; *Ph. C.* xxxiv. pp. 110, 237); less severe cases were all easily cured. In severe cases the mortality was 45 per cent.

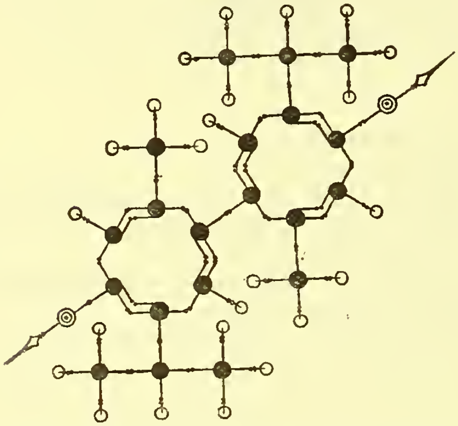
Fig. 970



Losophan, tri-iodo-cresol (*vide* fig. 429, p. 95), $C_7H_5I_3O$; m.p. 121°; used in cases of *Herpes tonsurans*, *Pityriasis versicolor*, &c. (*Therap. Monatsh.* 1892, p. 544)

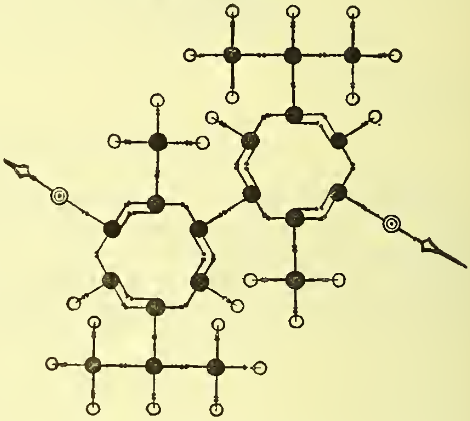
Besides this regular substitution of hydrogen-atoms in the benzene-ring, a replacing of the hydrogen in the hydroxyl is possible; the structure of the following three compounds have been thus interpreted by their compounders:

FIG. 971



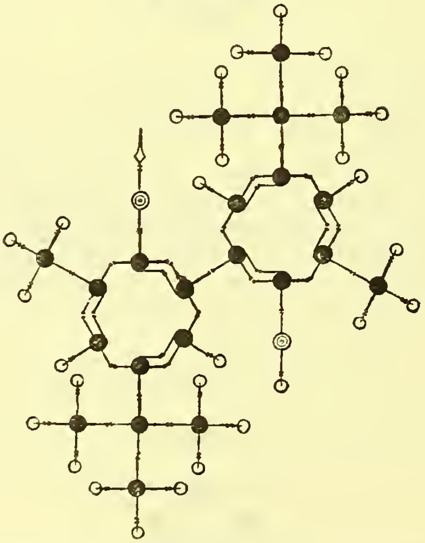
Aristol, thymolol, dithymol-iodide, originally called anniladin, $C_{20}H_{24}I_2O_2$; antiseptic; substitute for iodoform, chrysarobin, &c. (comp. fig. 458, p. 105)

FIG. 972



Carvacrol iodide, $C_{20}H_{24}I_2O_2$ (comp. fig. 459, p. 105); analogous to aristol

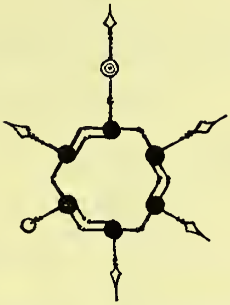
FIG. 973



Europhene, isobutyl-*o*-cresol-iodide, $C_{22}H_{29}IO_2$; m.p. about 110°; comp. fig. 460, p. 105 (*Ph. Ztg.* 1891, p. 440, through *Ph. C.*; the structural formula as there propounded is not in accord with the law of linking; I have therefore found it necessary to make an alteration as regards the position of iodine in the illustration); antiluetic and antiseptic; substitute for iodoform

The position given to iodine in these structures is so abnormal that they would have to be rejected if it were not for two or three compounds, in which iodine has been assigned a similar position; *e.g.* tetra-bromol-phenol-bromide, the structure of which can scarcely be any other than this:

Fig. 974



Tetra-bromo-phenol-bromide, $C_6HBr_5O$; m.p. 118° (*R. & S.* III. p. 139, and *Beilst,* ii. p. 436)

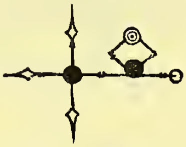
The only other way to place the bromine is to arrange it directly on the benzene-ring, exchanging places with the one hydrogen-atom; but that arrangement belongs to another compound, penta-bromo-phenol, with m.p. 225°, and altogether differing properties; therefore there is no alternative, though it has certainly long been considered a member of the suspected fraternity, to which, perhaps, some more iodine-compounds belong, all of which have been prepared for the purpose of superseding iodoform. Such compounds are *di-iodo-phenol-iodide*, *di-iodo-resorcin-iodide*, and *iodo-salicyl-iodide.*

In the form in which these compounds are represented above they must be looked upon as ether-formations of the respective phenols and hypo-iodous acid, a hypothetical body which has its analogue in hypochlorous acid (*vide* fig. 1630, p. 485), *Ber.* xxvi. p. 154; but very recent researches (*Ber.* xxv. pp. 2632, 3495, and xxvi. pp. 1307, 1354, June 1893) have brought to light a whole series of apparently analogous compounds, in which the group IO is bound to the benzene nucleus, not by the oxygen, but by the iodine, which, in consequence, appears in this combination, not as a monad, but as a triad, the group $-I=O$ (*iodoso-group*), representing the radical of the, also hypothetical iodous acid (comp. chlorous acid, fig. 1631, p. 485). These compounds have therefore been termed *iodoso-compounds*, and their formation may be looked upon as a combination of a benzene and the hypothetical iodous acid with elimination of water. The most remarkable circumstance is, however, that the iodoso-group acts like a strong base (*Ber.* xxvi. p. 1360). The result of still later researches, putting a different complexion on these compounds, will be found on p. 485.

## Aldehyde-derivatives

Chlorine can replace one, two, or three hydrogen-atoms of acetic aldehyde (fig. 538, p. 131). The last substitution-product, tri-chlor aldehyde (or rather its combination with water), has become widely known as chloral:

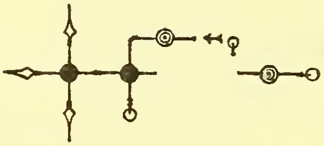
Fig. 975



Chloral, $C_2HCl_3O$; b.p. 97°·7

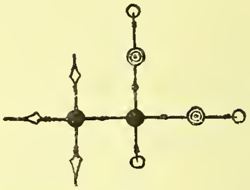
It forms with water a hydrated compound having two hydroxyls attached to the same carbon-atom, one of the rare cases of this occurrence:

Fig. 976



Chloral and water

Fig. 977

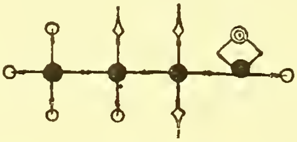


Chloralhydrate, $C_2H_3Cl_3O_2$ ; m.p. 57°

Bromalhydrate is an analogous compound with bromine instead of chlorine, $C_2H_3Br_3O_2$, b.p. 53°·5. Its therapeutic action is similar to that of chloral; its hypnotic effect, however, is not so marked. Used mostly as a sedative and antispasmodic in epilepsy, chorea, &c.

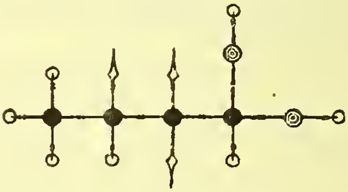
Analogous to this are the chlorine-derivatives from butyr-aldehyde (fig. 543, p. 132), or croton-aldehyde (fig. 549, p. 133):

Fig. 978



Trichloro-butyr-aldehyde, butylchloral,
$C_4H_5Cl_3O$ ; b.p. 164°

Fig. 979

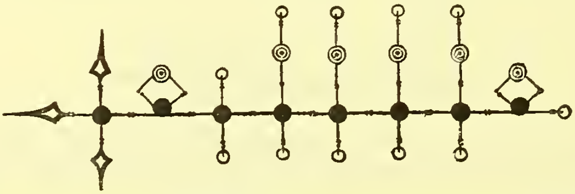


Butyl-chloralhydrate, croton-chloralhydrate,
$C_4H_7Cl_3O_2$ ; m.p. 78°

Hypnotic, anæsthetic, and sedative in trigemini neuralgia; externally for toothache with equal parts of carbolic acid

Chloral may be joined to glucose to form a glucoside-like compound:

Fig. 980



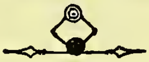
Chloralose, $C_8H_{11}Cl_3O_6$ ; m.p. 186° (*Ber.* xxii. p. 1050; *Compt. Rend.* cxvi. 1893, p. 63); a more powerful hypnotic than chloral, but increases the irritability of the spinal cord. Another structure with ring formation, in which tri-chloro-methyl and part of glucose form side-chains, has been suggested. An isomer, para-chloralose, m.p. 227°, has also been prepared (*Compt. Rend.* cxvii. p. 734)

# Acid-derivatives

Hydrogen-atoms in the alkyl-body (including closed chains) of the acids may, one after the other, be replaced by halogens; carboxyl's hydrogen cannot be so replaced, whereas carboxyl's hydroxyl can.

From *carbonic acid* (fig. 690, p. 179) is thus formed

FIG. 981



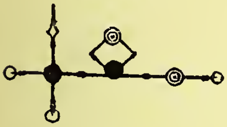
Phosgene, carbon-oxy-chloride, carbonyl-chloride, $CCl_2O$; a gas; b.p. 8°

It is formed in chloroform by exposure to light for several months, and is suggested as the probable cause of death during chloroform anæsthesia (*Ch. & D.* 1892, p. 221). This hypothesis is, however, not well supported, physiological researches having given contradictory results, disclosing also a certain connection between fatal cases and the amount of alkaloïdal substances present in the urine (Dr. Lauder Brunton's inaugural address at the meeting of the Pharmaceutical Society of Great Britain, October, 1893).

Chloro-carbonic acid (*chloroformic acid*), Cl-CO.OH, is carbonic acid in which one hydroxyl only is substituted by chlorine. It cannot be isolated, as it breaks up into hydrochloric acid and carbon dioxide; nor have any salts been prepared, but several compound-ethers are known.

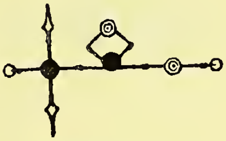
From *acetic acid*:

FIG. 982



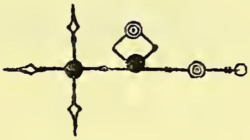
Monochlor-acetic acid, $C_2H_3ClO_2$; m.p. 63°

FIG. 983



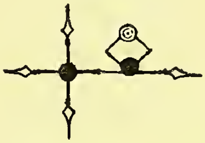
Dichlor-acetic acid, $C_2H_2Cl_2O_2$; b.p. 191°

FIG. 984



Trichlor-acetic acid, $C_2HCl_3O_2$; m.p. 52°·5

FIG. 985

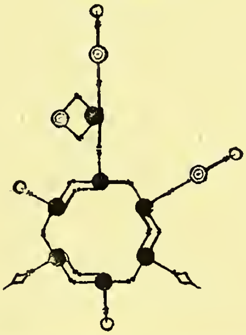


Trichlor-acetyl-chloride $C_2Cl_4O$; b.p. 118°

All these compounds are caustics, some of them used for the removal of corns and warts.

From *aromatic acids* we shall mention

FIG. 986



Di-iodo-salicylic acid, $C_7H_4I_2O_3$; m.p. 220° (decomp.); analgesic, antithermic, antiseptic, heart-paralysing

## Future Nomenclature of Halogen-compounds

The rules for numbering carbon-atoms in hydrocarbons are also applied to their substitution-products. In chains with no side-chains and no triple or double bindings the numbering commences at the end most proximate to a substituent, and when two substituents are placed equidistantly from each end, the one is chosen where the substituent is of a higher order; or, in the case of substituents of equally high order, the one which has the lowest atomic or molecular weight.

Accordingly, chloral (fig. 975, p. 271) becomes *tri-chlor-ethanal*, chloral-hydrate (fig. 977, p. 272) 2 *tri-chlor-ethane*-1 *diol*, butyl-chloral-hydrate (fig. 979, p. 272) 2 : 2 : 3 *tri-chlor-butane*-1 *diol*, mono-chlor-acetic acid (fig. 982, p. 273) *chlor-ethane* (or *ethanoïc*) *acid*, &c.

# PART IX.

# Sulphur Compounds

# Sulphur-compounds

*Index*, Ⓢ *Chemical symbol*, S.

The next element which serves to form new compounds is sulphur. We meet here with an element that behaves towards other elements, as regards its power to combine with them, in a way different from what we have, as yet, seen of carbon, hydrogen, oxygen, and halogens.

We have been led to believe that each of these elements has a certain number of valencies, no more, no less; and that these valencies are always in activity, must combine with some other valencies, and that a compound is not at rest, i.e. in a stable form, until the cravings of all valencies have in one form or another been satisfied. This is, however, truth with modifications.

It is true as regards hydrogen in all its combinations. Hydrogen is a monad, and remains a monad under all circumstances that we know of.

It is true as regards carbon in all its relations to hydrogen, provided we admit the theory of double and triple bonds as truths.

It is true as regards oxygen in all its known combinations, and it is true as regards halogens in the combinations which we have as yet discussed.

Before we go on with this subject it is desirable to explain what is understood by *electro-positive* and *electro-negative* bodies, not so much because I consider expressions which have been used for at least fifty years, unfamiliar, but that I seize the opportunity of presenting (in a popular and much condensed form) the latest views on molecules' and atoms' behaviour towards heat, electricity, and in solution.

All bodies can exist in three states of aggregation—in the solid, liquid, or gaseous state—provided they do not decompose by heat. The molecules of a solid are all under the influence of each other; they cannot move about as they like, each particular molecule being within the sphere of action of all its neighbours. In the liquid state, however, they can move about more freely, although they do not leave each other entirely, but wander about from one to another. In the gaseous state each molecule is beyond the attractive force of any other, and starts away along its own path, which is a straight one, until altered by its colliding with another molecule, or rebounding from some impassable boundary. In all these aggregates, even in the solid one, the molecules are moving about, and will on reaching the surface of the body exert a certain degree of pressure on the enclosing boundaries. In the case of solid bodies the particles are held together with so much force that scarcely any of them can escape, even if the enclosing medium—air, for instance—would allow their passage. It is like a ball fastened to a string being whirled round, and coming too near a window will manifest its power of pressure by smashing the glass, but without being able to gain its liberty through the aperture it has made, except when the string may, now and then, be cut by the broken glass. In liquids this bond is so much loosened that many of the particles coming to the surface can free themselves from the restraint of the others, and move away into space, i.e. they assume the conditions of the gaseous state (evaporation).

We know that all bodies, with the exceptions mentioned, can exist in these three states of aggregation, and we know from daily experience that the conversion from one into another of these states is effected by adding or abstracting heat. But heat is motion; so it appears intelligible enough that when we add motion to motion it will increase, and consequently lessen more and more the attracting bond between molecule and molecule.

But it is not the molecules only that are moving; the several atoms of which a molecule consists have a motion of their own, which is similarly affected by the motion we call heat. As soon as heat has made the molecules independent one of another, in other words converted the body into the gaseous state, the effect of heat begins to tell upon the atomic motion by increasing its speed, and thereby loosening, and at last breaking, the bond that holds them together, splitting the molecules gradually up into smaller and smaller fragments or groups according to the more or less complex nature of the compound, and finally into single atoms: this process is termed dissociation.

The molecules in a gas have not all the same motion or heat, in consequence of their irregular collisions. When we measure the motion or heat by a thermometer it only gives us the average heat of those molecules with which it is in contact; some may have a higher, others a lower temperature. Those which have the highest temperature commence first to break up, and gradually, as more and more heat is added, the others follow their example.

Water, for instance, having been transformed by heat into gas, undergoes first chemical exchange, forming molecules of oxygen and hydrogen.

Fig. 987

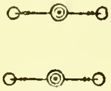
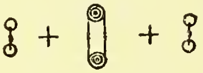


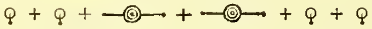
Fig. 988



$2(H_2O) = H_2 + O_2 + H_2$

and on further heating these molecules separate, forming a mixture of free atoms:

Fig. 989



At 3000° the separation of all water-molecules is accomplished; therefore we know that no steam can exist above that temperature.

In hydrocarbons much less heat is required to enable the hydrogen atoms to separate from the carbon than to make the carbon atoms themselves separate from one another. That is the reason of double bonds being formed so frequently at high temperatures.

The temperature at which dissociation may be regarded as accomplished varies very much with the different compounds, some being dissociated at ordinary temperature (carbon monoxide and nitric oxide [1]), others at temperatures which we cannot produce, but are supposed to exist on the sun, where all elements may be considered present as free atoms until they, hurled away into space, cool sufficiently to form molecules, and fall down upon the sun, to be again dissociated, the process continually repeating itself and giving rise to those movements on the sun's surface which we compare to violent storms and cyclones, and to those phenomena which we describe as sun-spots, faculæ, prominences, &c.

The same sort of dissociation also takes place in solutions when solid bodies are dissolved in liquids, or even in other solid bodies, as they are in steel, glass, alloys, &c. The bonds between the molecules and atoms are so much loosened by coming into contact with the dissolving body that one by one they tear themselves away from the rest and commence their wandering through the other body just like the molecules of a gas. It is, in fact, a perfect evaporation of one body into another, just as a liquid voluntarily evaporates into the air. As a striking instance of these movements in solid bodies may be mentioned copper-plated zinc; the copper gradually penetrates into the zinc and at last leaves the surface quite white as it was before it was coppered.

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[1] These compounds have a very low boiling-point, somewhere about −200° (carbon monoxide's m.p. −199°), and it is probable that they in the fluid state double the number of atoms in the molecule. Carbon monoxide, for instance, is as a gas composed of one atom of carbon and one atom of oxygen, CO leaving two of carbon's valencies free. In the fluid state the molecule will probably consist of two such groups, $O=C=C=O$, when all the valencies are engaged; similarly with nitric oxide, $O=N-N=O$.

We know that a molecule in a gas rushes about in all directions, frequently coming in contact with other molecules from which it rebounds, continuing its path in one direction until a fresh collision gives it a new one. But of course a certain proportion of them will, if the gas is enclosed in a vessel, reach and strike the wall of that vessel, and consequently exert a pressure on it. Exactly the same process takes place in a solution, a certain number of the molecules rushing about in a solvent, reach and strike the sides of the vessel in which it is contained. The pressure exerted by these impacts is styled the osmotic pressure, and, when measured by a suitable apparatus, has been found to be the same for different compounds when they are present in the same number of molecules, all other circumstances being equal. Consequently when we have ascertained the pressure of 342 grammes of cane-sugar (whose molecular weight we suppose to be known) in a litre of water, and find that 150 grammes of tartaric acid (whose molecular weight we suppose to be unknown) also dissolved in a litre of water exerts the same pressure, then, knowing 342 to be the molecular weight of the sugar, the molecular weight of tartaric acid must be 150. It has further been discovered that the freezing-point of a fluid is depressed to a certain degree when it contains in solution another compound, and the same law has been found to hold good in this case as in that of osmotic pressure, viz. that the depression of the freezing-point is the same for corresponding molecular weights of different compounds. This is used as a method of determining the molecular weight, and is known as Raoult's law.

There are, however, a considerable number of exceptions to this law, compounds that depress the freezing-point twice or three times as much as they should do according to their molecular weight. In order to explain this fact the hypothesis has been propounded and generally accepted as correct, that these compounds dissociate in solution, and that consequently for each molecule in the compound there are two or three &c. fragments of it present. Common salt, for instance, which is composed of one atom of chlorine and one atom of sodium, would, dissolved in water, split up into its components. The effect of this on the freezing-point would therefore be doubled, and that agrees with the fact. It is, however, not to be understood as if sodium- and chlorine-atoms were swimming about without taking the slightest notice of each other, an apprehension capable of producing cold perspiration on a chemical brow; on the contrary, there is an incessant joining and separating of the two elements' atoms, an unintermittent composition and decomposition of chloride of sodium. We may perhaps best picture the process to ourselves by thinking of a figure in certain dances called the grand chain, where ladies go one way and gentlemen the other, seizing alternately each other's right and left hands, but not letting go one hand before the next one has been taken hold of, continually changing partners without for a moment breaking the ring.

Further it has been discovered that all the compounds which form the exceptions from Raoult's law behave differently from what all the compounds that follow the law do towards an electric current.

The ends of the wires leading to and from a voltaic battery when dipped down in a vessel (the *electrolytic cell*) containing a liquid are termed *electrodes*. The one connected with the copper- or carbon-plate, the positive pole in the battery, is the *anode*, the other connected with the negative zinc-plate is the *kathode*. If the vessel contains a substance that follows Raoult's law no current will go through the liquid, and everything will remain just as it was before the electrodes touched the liquid. But if the vessel contains a liquid, or a solid in solution which forms an exception to that law, the current will pass through, and the liquid (*electrolyte*) will at the same time undergo decomposition (*electrolysis*).

Suppose common salt (one of the exceptions) were dissolved in the water; it would more or less, according to concentration and temperature, split up into free atoms of sodium and chlorine, running about in the water as already described. When now the electrodes are put down in the solution, the sodium-atoms nearest to the anode at the moment of closing the current will be loaded with positive electricity, with which they will swim over to the kathode, drop anchor, and discharge their cargo, which then returns to the battery through the kathode, leaving behind the sodium still at anchor. Atom upon atom arrive heaping up sodium at the kathode, each atom carrying a fixed load of electricity; therefore the quantity of electricity passed through an electrolytic cell can be determined by the quantity of metal deposited on the kathode (such meters are used for measuring the quantity of electricity supplied to houses; as the electricity is only carried through from one electrode to the other none of it is lost on its way through the electrolytic cell). Similarly, the chlorine-atoms are loaded at the kathode with negative electricity, which it carries to the anode, where it is forwarded to the battery, the chlorine-atoms remaining behind as did the sodium at the other electrode,[1] always keeping in mind please 'the grand chain.'

The fragments into which the original compound is split up by dissociation are collectively termed ions, those congregating at the anode being called anions, those at the kathode kathions. The anions are said to have electro-negative, the kathions electro-positive character. The process itself is called electrolysis.

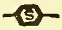
We are now prepared to conclude our discussion of the valencies of elements, which we broke off after having remarked that hydrogen was under all circumstances a monad, carbon a tetrad (with one only exception, carbon monoxide), oxygen a dyad, and halogens monads, in all combinations hitherto discussed.

But the halogens are only monads in their combinations with elements more electro-positive or less electro-negative than they themselves are; towards oxygen, however, they may present one, three, five, or seven valencies, according to the circumstances under which they combine with that element.

Similarly with sulphur. Towards electro-positive elements or groups it is a dyad with two valencies, but towards electro-negative bodies it shows, according to circumstances, four or six valencies.[2] We shall therefore have to consider the combinations of sulphur under different headings: first, those with positive bodies in which sulphur appears as a dyad; secondly, those with negative bodies in which sulphur will be considered separately according to its tetrad or hexad nature.

# DYAD SULPHUR-COMPOUNDS

## Thio-compounds

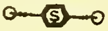
*Index,* 

In its electro-negative character sulphur always appears as a dyad, and has such a remarkable resemblance to oxygen in its chemical behaviour that it may often be looked upon as replacing oxygen in its several compounds. All these are termed thio-compounds.

## Sulphur and Hydrogen

In water, our very first oxygen-compound, sulphur may take the place of oxygen:

Fig. 990



Sulphuretted hydrogen, $H_2S$; a gas; present in sulphureous springs

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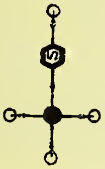
[1] This is not strictly correct, as, in point of fact, neither sodium nor chlorine is to be found at any of the electrodes on account of a secondary decomposition, with which we shall not complicate the matter.

[2] Lately a sulphuric acid has been prepared consisting of one sulphur-atom and four oxygen-atoms; if that is found to be correct, sulphur may have even eight valencies.

## Thio-alcohols, or Mercaptans

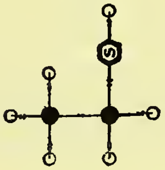
Also in *alcohols* (*vide* p. 67) sulphur may replace oxygen, giving rise to a series of compounds which have received the special name of mercaptans, other names being alkyl-sulphhydrates, thio-alcohols, and thiols. Examples are

FIG. 991



Methyl-mercaptan, methyl-hydrosulphide, $CH_4S$; b.p. 6°, according to most authorities; *Beilst* (i. p. 340) has 20°, and Weyl 148° (probably a misprint)

FIG. 992



Ethyl-mercaptan, ethyl-hydrosulphide, $C_2H_6S$; b.p. 36°

The latter is the cause of the peculiar smell of urine after partaking of asparagus (*Arch. exp. Pathologie*, xxviii. p. 206), the former is one of the gases in the intestines

The hydrogen in connection with sulphur may in analogy to *alcoholates* (*vide* p. 109) be replaced by metals, the ensuing compounds being termed mercaptides.

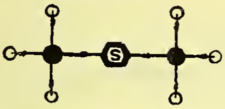
Sulphur can likewise replace oxygen in *phenols* (p. 92), forming thio-phenols or phenyl-mercaptans.

## Thio-ethers, or Alkyl- (phenyl-) sulphides

These compounds correspond to the ethers (p. 113), and may be considered derivatives of them by substitution of sulphur for oxygen.

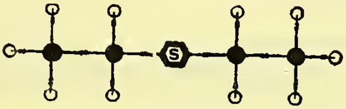
Thus to *methyl-* and *ethyl-ether* (figs. 471 and 473, p. 113) correspond

FIG. 993



Methyl-sulphide, $C_2H_6S$; b.p. 41°

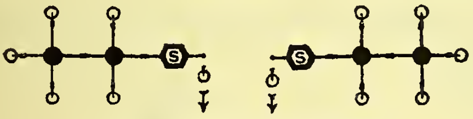
FIG. 994



Ethyl-sulphide, $C_4H_{10}S$; b.p. 92°

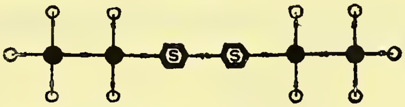
By removing a hydrogen-atom from each of two molecules of mercaptans, we obtain di-sulphides, to which there is no corresponding compound among the oxygen derivatives (except, perhaps, two superoxides of acid radicals, acetyl- and butyryl-superoxide), *e.g.*

FIG. 995



Two molecules of ethyl-sulphide

FIG. 996



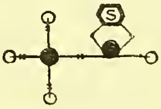
Ethyl-di-sulphide, $C_4H_{10}S_2$; b.p. 153°

Similarly, phenyl-di-sulphide is formed from two molecules of thio-phenols or phenyl-mercaptans.

## Thio-aldehydes

The same displacing of oxygen takes place in *aldehydes*,

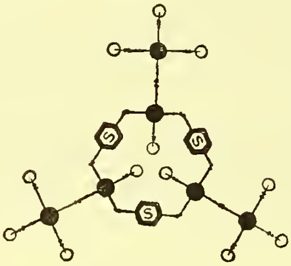
FIG. 997



Thialdehyde, $C_2H_4S$

but it has not yet been isolated free from other compounds that accompany its formation. It will, however, polymerise exactly as aldehyde forms paraldehyde (*vide* fig. 540, p. 131).

FIG. 998



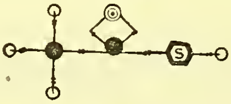
Parathialdehyde, $C_6H_{12}S_3$; m.p. 101°; a hypnotic

It may also be considered a benzene-ring with sulphur-atoms, replacing carbon-atoms in the ring, analogous to oxygen in paraldehyde.

## Thio-acids

Sulphur can replace oxygen in hydroxyls of *acids*, both carboxylic and alcoholic hydroxyls, but not, so far as we at present know, the oxygen in carbonyl, except in carbonic acid.
Thus we have

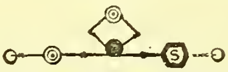
FIG. 999



Thiacetic acid, $C_2H_4OS$; b.p. 93°

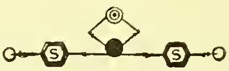
From *carbonic acid* the following substitutions by sulphur are known, though most of them in derivatives only:

FIG. 1000



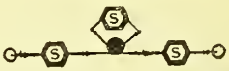
Thioxy-carbonic acid, carbonyl-thioxy-acid, $CH_2SO_2$

FIG. 1001



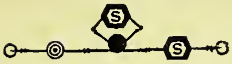
Di-thioxy-carbonic acid, carbonyl-di-thio-acid, $CH_2S_2O$

FIG. 1002



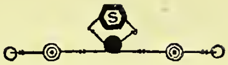
Tri-thio-carbonic acid, sulpho-carbonic acid, $CH_2S_3$; a brown oily liquid

Fig. 1003



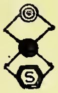
Oxy-di-thio-carbonic acid, $CH_2S_2O$

Fig. 1004



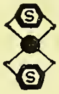
Di-oxy-thio-carbonic acid, $CH_2SO_2$; b.p. 161°; oily liquid

Fig. 1005



Carbon-oxysulphide, CSO; a gas

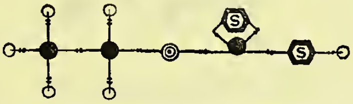
Fig. 1006



Carbon-di-sulphide, $CS_2$; b.p. 46°

Many derivatives of these compounds are known, principally compound ethers (p. 231). The acid compound-ethers of *oxy-di-thio-carbonic acid* are known by the name of xanthic acids:

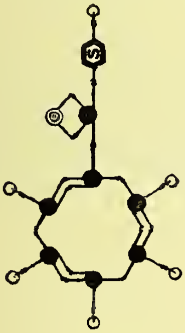
Fig. 1007



(Ethyl-) Xanthic acid, $C_3H_6S_2O$; decomposes on slightly heating (25°); its potassium salt is used as a phylloxera-killer

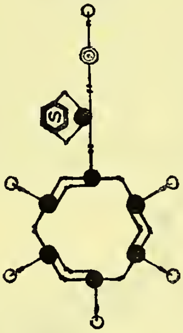
Similarly, sulphur can displace the oxygen-atoms in carbonic acid when this acid forms part of *aromatic compounds*; for instance, in *benzoic acid.*

Fig. 1008



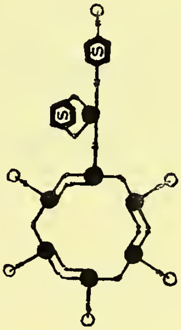
α-Thio-benzoic acid, $C_7H_6SO$
m.p. 24°

Fig. 1009



β-Thio-benzoic acid, $C_7H_6SO$
crystals

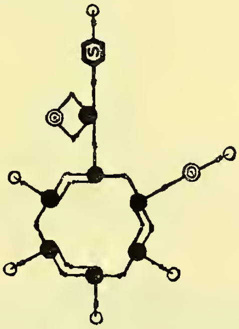
Fig. 1010



Di-thio-benzoic acid, $C_7H_6S_2$;
an oily liquid; easily decomposes

and in *salicylic acid*:

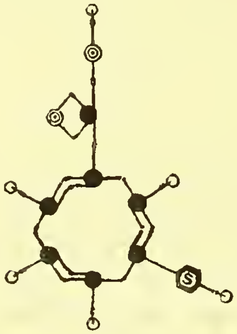
Fig. 1011



Thio-salicylic acid, $C_7H_6SO_2$; brown amorphous mass

In *hydroxy-benzoic acids* (p. 216) the oxygen in the hydroxyls may likewise be replaced by sulphur; thus we know

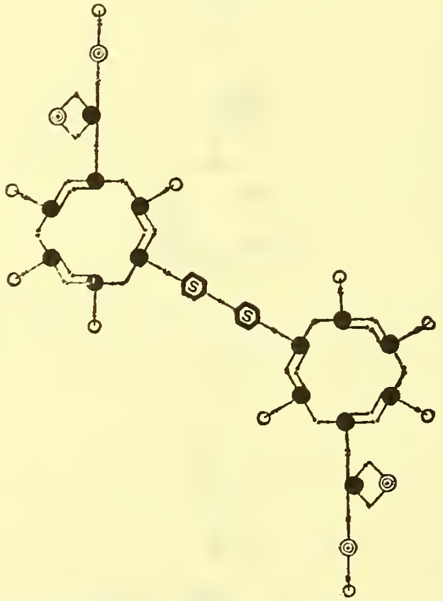
Fig. 1012



Meta-thio-hydroxy-benzoic acid, $C_7H_6SO_2$; m.p. 146°

Two of these can combine by eliminating the sulphurs' hydrogens:

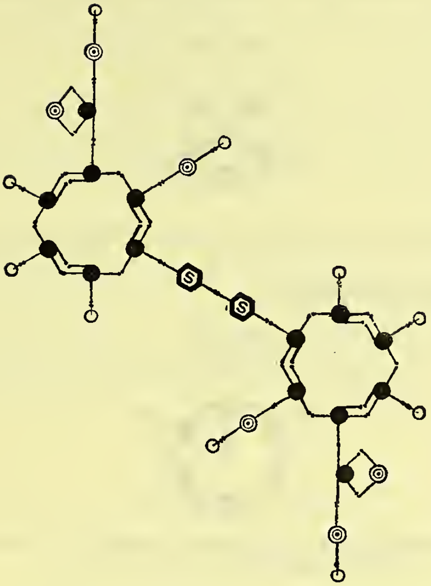
Fig. 1013



Meta-di-thio-hydroxy-benzoic acid, $C_{14}H_{10}S_2O_4$; m.p. 242°

A similar compound may be (theoretically) derived from *di-hydroxy-benzoic acids*. We know two of them, though the exact position of the sulphur-group has not been ascertained. For the sake of illustration, we represent one of them, analogous to the preceding one.

Fig. 1014



Di-thio-salicylic acid, $C_{14}H_{10}S_2O_6$; a thick oily liquid.

The other acid is an isomer; the sodium salts of these two acids are distinguished, one as No. I. and the other as No. II.; the mixed salts have the trade name dithion, which is used as an antiseptic in articular rheumatism and gonorrhœa.

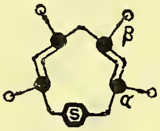
Thioform is the analogous basic bismuth salt recommended in many cases as a substitute for iodoform (*Repert. d. Thierheilk.* vi. 1893).

## Thiophene

We have seen oxygen helping to close a chain in furfurane (fig. 941, p. 260) and pyrone (fig. 945, p. 260).

Sulphur can perform the same task:

Fig. 1015

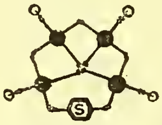


Thiophene, $C_4H_4S$; b.p. 84°; present in coal tar

Thiophene is a compound that very much resembles benzene. Its combination with two atoms of iodine, thiophene-di-iodide, has been recommended as a substitute for iodoform, being non-poisonous (*Wiener med. Presse*, *Ph. C.* xxxiv. p. 112).

The heat of combustion not indicating any double-bonds in thiophene, diagonal bonds have here too been suggested,

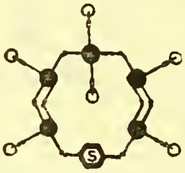
Fig. 1016



analogous to those proposed for benzene, fig. 290, p. 55; what is said there about this sort of bonds holds good here too.

A hexagonal form has also been prepared:

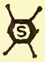
Fig. 1017



Penthiophene, $C_5H_6S$; penthiophene has not yet been isolated, but a methyl-derivative is known (*Die Thiophengruppe*, by V. Meyer)

The methylene-group in para-position has also been substituted by sulphur in the compound biophene, $C_4H_4S_2$, b.p. 170°.

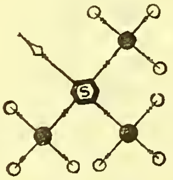
# TETRAD SULPHUR-COMPOUNDS

*Index*, 

## Sulphines

If one of the valencies is occupied by an electro-negative mono-valent element or group (*e.g.* iodine), four, altogether, of the valencies of sulphur will be excited to activity, so as to admit the connection of three hydrocarbons instead of two in alkyl-sulphides (p. 281):

Fig. 1018



Tri-methyl-sulphine-iodide, $C_3H_9IS$; crystals

This compound behaves like a salt; but if iodine is replaced by hydroxyl, the product tri-methyl-sulphine-hydroxide is then a powerful base, as strong as caustic potash.

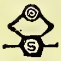
# Oxygen-compounds of Sulphur

Oxygen and sulphur unite in many proportions, sulphur acting sometimes as a tetrad, sometimes as a hexad. We have not to do with all of them in organic chemistry, and only those with one, two, three, or four atoms of oxygen will be spoken of here.

## OXY-SULPHINES AND SULPHINIC ACIDS

As a tetrad, sulphur can combine with one oxygen atom, leaving the two remaining free valencies to combine otherwise. The radical of these compounds is termed

Fig. 1019



Oxy-sulphine, SO

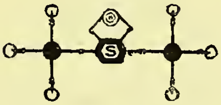
If both free valencies are united to carbon-atoms the compounds are known as sulphine-oxides or sulphoxides; if only one valency is united to a carbon-atom and the other to a hydroxyl, we call the compound a sulphinic acid. If both valencies are connected with hydroxyls, it is termed symmetric sulphurous acid.

Oxy-sulphine, being a radical, does not, of course, exist in the free state; sulphinic acid and symmetric sulphurous acid have not themselves been isolated, being converted into sulphurous anhydride. They are all known chiefly through their derivatives or as salts.

Some of these are

### Sulphine-oxide's Derivative

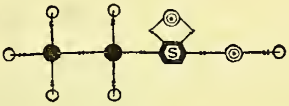
Fig. 1020



Di-methyl-sulphine-oxide, di-methyl-sulphoxide, $C_2H_6SO$; an oily liquid

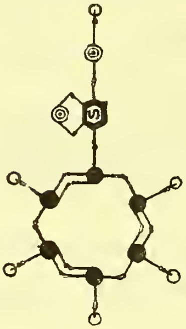
### Sulphinic Acid's Derivatives

Fig. 1021



Ethyl-sulphinic acid, $C_2H_6SO_2$; syrupy liquid

Fig. 1022



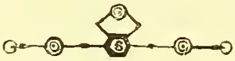
Benzene-sulphinic acid, $C_6H_6SO_2$ ; m.p. 83°

Some authorities look upon sulphur in these compounds as a hexad, and place the oxygens on each side of the sulphur in the form of sulphone (fig. 1029) and the hydrogen in direct connection with sulphur.

## Symmetric Sulphurous Acid's Derivatives

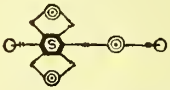
Sulphurous acid does not exist in the free state, but is supposed to be present in derivatives in either of the two following structurally different forms:

Fig. 1023



Symmetrical sulphurous acid, $SH_2O_3$

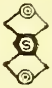
Fig. 1024



Asymmetrical sulphurous acid, $SH_2O_3$

It assumes in its combinations such form as is best suited to the circumstances. But both forms when liberated lose a molecule of water, and are converted into sulphurous anhydride.

Fig. 1025



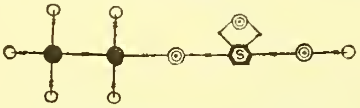
Sulphurous anhydride, sulphur dioxide, $SO_2$ ; a gas

The process is analogous to that of carbonic acid, being converted into carbon dioxide (fig. 711, p. 184).

In the first form sulphur is a tetrad; in the second it is a hexad, and therefore not to be dealt with just now.

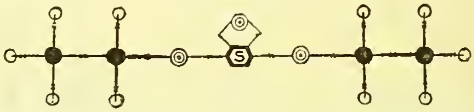
The symmetrical acid's derivatives are characterised by their instability. They form neutral and acid compound-ethers (p. 231), the latter being incapable of existence in the free state, but a potassium salt is known; also some neutral ethers. They are all readily saponified by water alone.

Fig. 1026



Ethyl-sulphurous acid, $C_2H_6SO_3$

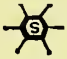
Fig. 1027



Ethyl-sulphite, $C_4H_{10}SO_3$ ; b.p. 161°. Compare the structure of the compound ethers of asymmetrical sulphurous acid (fig. 1054, p. 295)

# HEXAD SULPHUR COMPOUNDS

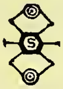
Fig. 1028

*Index,* 

The hexad sulphur unites with two atoms of oxygen, leaving two free valencies at liberty to combine with two mono-valent radicals.

This combination of sulphur and oxygen is spoken of as a radical, and is termed sulphuryl or sulphone:

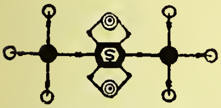
Fig. 1029



Sulphuryl or sulphone

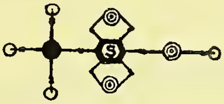
With carbon-atoms attached to both free valencies the derivatives are termed sulphones; with a carbon-atom on one side and a hydroxyl on the other they are styled sulphonic acids; with a hydrogen-atom on one side and hydroxyl on the other it is asymmetrical sulphurous acid; and with hydroxyls on *both* sides it is sulphuric acid.

Fig. 1030



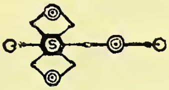
Dimethyl-sulphone, $C_2H_6SO_2$; m.p. 109°

Fig. 1031



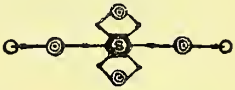
Methyl-sulphonic acid, $CH_4SO_3$; syrupy liquid; decomposes above 130°

Fig. 1032



Asymmetrical sulphurous acid, $SH_2O_3$; does not exist in the free state

Fig. 1033

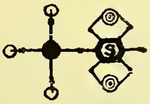


Sulphuric acid, $SH_2O_4$; b.p. 338°

## Sulphone Compounds

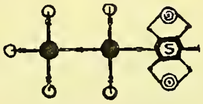
Sulphone itself is a di-valent radical; when we join a hydrocarbon to one of its two free valencies, the product is a mono-valent radical:

Fig. 1034



Methyl-sulphone, $CH_3SO_2$

Fig. 1035

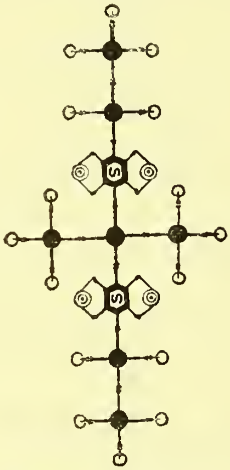


&c.

Ethyl sulphone, $C_2H_5SO_2$

These radicals may be affixed to many hydrocarbons and their derivatives, whether with open or closed chains. One that has gained much notoriety is propane, through having two of its hydrogen-atoms replaced by ethyl-sulphone:

Fig. 1036



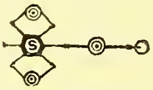
Sulphonal, di-methyl-di-ethyl-sulphone-methane, $C_7H_{16}S_2O_4$; m.p. 125°; an excellent hypnotic

Several efforts have been made to improve upon sulphonal by replacing one of the methyls by ethyl (trional) or both methyls by ethyls (tetronal), or by adding a third ethyl-sulphone to sulphonal (tri-ethyl-sulphone-methyl-methane), but without success. Also substitution of one or more hydrogen-atoms by chlorine has been tried with the same result.

## Sulphonyl Compounds

When a hydroxyl is added to one of sulphone's free valencies we have the mono-valent radical of sulphonic acid, sulphonyl:

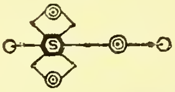
Fig. 1037



Sulphonyl, $SHO_3$

When a hydrogen is added on the other side, the hypothetical sulphurous acid (*asymmetrical*) is formed.

Fig. 1038

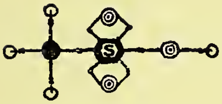


Asymmetrical sulphurous acid, $SH_2O_3$

The radical of sulphonic acid can be joined to hydrocarbons, both with open and closed chains, or their derivatives, forming acids (sulphonated).

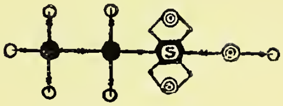
## Derivatives from Open Chains

Fig. 1039



Methyl-sulphonic acid, $CH_4SO_3$; syrupy fluid; decomposes on heating

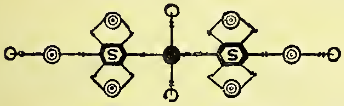
Fig. 1040



Ethyl-sulphonic acid, $C_2H_6SO_3$; deliquescent crystalline mass; decomposes at a high temperature, and is not saponifiable (compare the structure of ethyl-sulphurous acid, fig. 1026, p. 288, which, being an ether, is saponifiable)

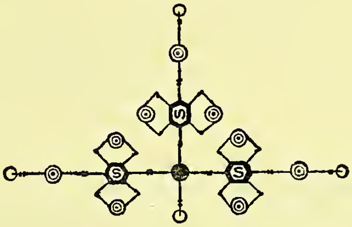
Two or three sulphonic acid radicals may join the same carbon in these hydrocarbons:

Fig. 1041



Methyl-di-sulphonic acid, $CH_4S_2O_6$; deliquescent crystals

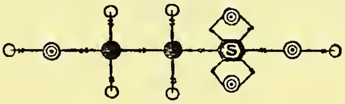
Fig. 1042



Methyl-tri-sulphonic acid, $CH_4S_3O_9$; crystals

As a derivative from *alcohol* or *glycol* (fig. 364, p. 76) may be considered

Fig. 1043

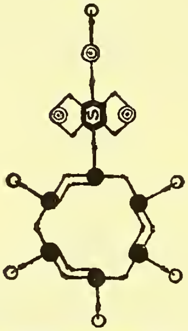


Isethionic acid, hydroxy-ethyl-sulphonic acid, $C_2H_6SO_4$; deliquescent crystals

## Derivatives from Benzene

While the radical of sulphonic acid is introduced into the open-chain compounds with some difficulty, or at least by a roundabout way only, it is characteristic of compounds with closed chains that they join the same radical most easily, and as directly as possible, by being treated with sulphuric acid. Consequently a great number of these compounds exist of which we shall mention a few.

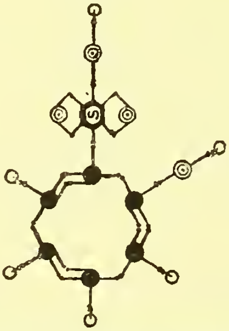
Fig. 1044



Phenyl- or benzene-sulphonic acid, $C_6H_6SO_3$ ; m.p. 40°

Benzene will also combine with two or three sulphonic acid-radicals, but does not seem willing to accept more than three, although some derivatives will take four—which is their present limit.

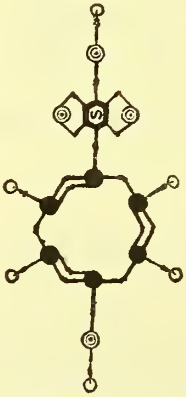
Fig. 1045



Aseptol, sozolic acid, ortho-phenol-sulphonic acid, $C_6H_6SO_4$ ; disinfectant and antiseptic, more powerful than carbolic acid or salicylic acid

On heating, the hydroxyl leaves its position and exchanges places with the hydrogen-atom in para-position (intramolecular change):

Fig. 1046

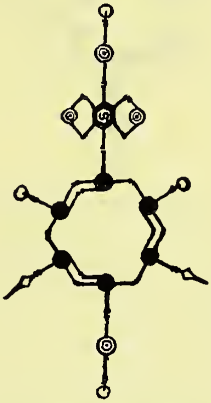


Para-phenol-sulphonic acid, $C_6H_6SO_4$ ; syrupy liquid

Sozal is the aluminium-salt of this acid (two atoms of aluminium engaging six molecules of the acid). Clinical and bacteriological experiments do not agree as to the value of this antiseptic.

Two hydrogens in the benzene-ring may be displaced by iodine-atoms:

Fig. 1047

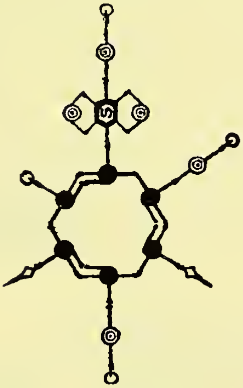


Sozoiodol, di-iodo-phenol-*p*-sulphonic acid, $C_6H_4I_2SO_4$

The acid itself is not employed for medicinal purposes, but its salts have found extensive use. The potassium- and sodium-salts (the metal replaces the hydrogen-atom in the sulphonic radical) are used as non-poisonous antiseptics in obstinate diseases of the skin, chronic catarrh of the nose, gonorrhœa, syphilis, cancer, rheumatism, &c.; salts with mercury, zinc, aluminium, magnesium, ammonium, lithium, silver, lead, &c., are in use.

When another hydroxyl is added to the above we have

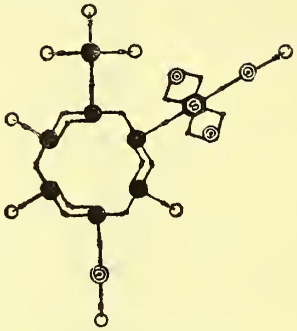
Fig. 1048



Picrol, di-iodo-resorcin-sulphonic acid, $C_6H_4I_2SO_5$; the potassium salt is used as an antiseptic

A *cresol-derivative* is

**Fig. 1049**



*p*-Cresol (p. 95) -*o*-sulphonic acid, $C_7H_8SO_4$ ; m.p. 98°·5

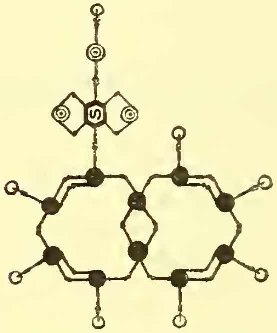
Four isomeric acids are structurally known ($CH_3 : OH : SHO_3$, 1 : 2 : 5, 1 : 2 : 4, 1 : 4 : 2, and 1 : 4 : 3), besides some others, the structures of which have not yet been ascertained.

They are all used as disinfectants.

Acidum sulpho-carbolicum crudum is made by treating crude carbolic acid with sulphuric acid. The crude carbolic acid consisting chiefly of cresols, the product will of course be mainly a mixture of different sulphonated cresols. As, however, these too are powerful disinfectants, it makes practically no difference.

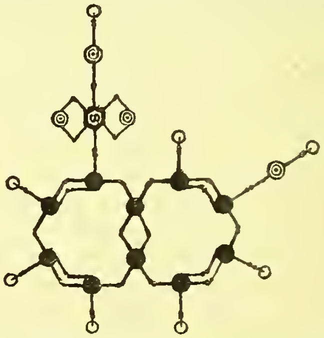
## Derivatives from Naphthalene

Fig. 1050



Naphthalene α-sulphonic acid, $C_{10}H_8SO_3$ ; m.p. 90°

Fig. 1051



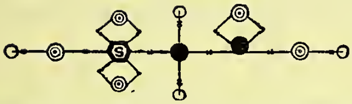
β-Naphthol α-sulphonic acid, croceïc acid, $C_{10}H_8SO_4$ ; decomposes on heating; its neutral calcium salt has recently been introduced by the name of asaprol as an antiseptic

Seven isomeric β-naphthol sulphonic acids are known.

Alumnol is the aluminium salt of β-naphthol-di-sulphonic acid: it is an astringent, can stop tears to any extent, and is therefore used in ophthalmic practice; also in gynæcologic and dermatologic cases, and in otorrhœa (*Ph. C.* xxxiii. p. 697).

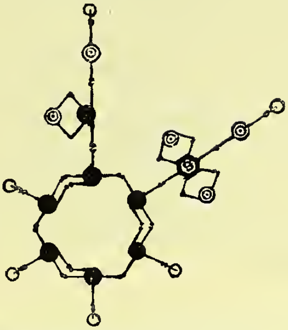
## Sulphonyl's Combinations with Acids

Fig. 1052



Sulpho-acetic acid, $C_2H_4SO_5$; m.p. 62°; strong di-basic acid; may be considered a combination of sulphonic acid with either acetic acid less $H_2$, or glycollic acid less $H_2O$

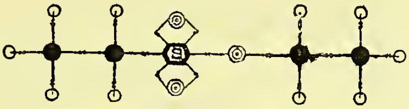
Fig. 1053



*o*-Mono-sulpho-benzoic acid, $C_7H_6SO_5$; m.p. 240° decomp.; mother-substance of the sweet saccharine (fig. 1308, p. 368)

The sulphonic acids, like other acids, form *compound ethers*:

Fig. 1054



Ethyl-sulphonic ethyl-ether, $C_4H_{10}SO_3$; b.p. 213°. Compare the structure of the compound ethers of symmetrical sulphurous acid (fig. 1027, p. 288)

Experience has taught us that the introduction of sulphur, in one form or the other, into various compounds produces therapeutically beneficial effects. Thus a very ancient remedy was linseed oil, in which sulphur had been dissolved by heating. More recently natural products have been found containing a large percentage of sulphur, and these have been utilised for the same purpose; prominent among them is a bituminous mineral, found somewhere in the Tyrol, called *stinking stone*, we may safely suppose, from the smell of it: it consists mainly of fossilised remains of fish from former ages. The destructive distillation of this bitumen yields a distillate separating into two oily layers, the lighter of which, purified by redistillation, is rich in sulphur (2·5 per cent.), but its constitution is unknown. This light oil is sulphonated by treating with sulphuric acid, after which it is neutralised with ammonia (formerly soda was used) and given the name of ichtyol. The acid is said to be dibasic, and its empirical formula to be $C_{28}H_{36}N_2S_3O_6$ (*Monatsh. f. pr. Dermat.* ii. p. 257), thus containing about 16 per cent. sulphur; no doubt it is a mixture of several thio-, sulphone-, and sulphonic compounds. It is a tar-like substance of herb-like odour. The raw oil is insoluble in water, and the object of sulphonating (as in most other cases where this operation is performed) is to make it soluble. A general characteristic of sulphonic acids (except those with long side-chains), and especially their salts, is their solubility in water, even when the mother-substance is quite insoluble. Ichtyol is partly soluble in water, entirely so in alcohol-ether.

It is used in psoriasis, eczema, and articular rheumatism, internally for catarrh of the stomach and lungs.

Of course, the success of ichtyol has called forth several attempts to displace it by artificial products.

Thiol (Ichtyolum germanicum) is one of them. It is prepared from the brownish paraffin- or gas-oils by first heating them with sulphur (10 per cent.) to form thio-compounds; afterwards, treating them with sulphuric acid, producing sulphonic acids, neutralising with ammonia, and converting them at last by evaporation into a form of either fluid or dry extract.

Tumenol is prepared from bituminous oils (sp. g. 0·86–0·89), from which phenols and acids have been removed by caustic soda, and bases by diluted sulphuric acid. The purified oil is then sulphonated; according to the degree of sulphonation, tumenolsulphone or tumenolsulphonic acid is obtained. Thus tumenol is not, like thiol, first sulphuretted (heated with sulphur to form thio-compounds), and contains for that reason less sulphur. It is a dark syrupy fluid, and is recommended for running forms of eczema, prurigo, and pruritus.

Thiolin is linseed oil, first sulphuretted, then sulphonated and neutralised with soda or potash.

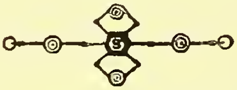
Thilanin is sulphuretted (but not sulphonated) lanolin.

Polysolve, *solvin*, may be prepared from olive-, almond-, castor-oil, &c., by treating them with sulphuric acid and neutralising with potash, soda, or ammonia; a soap-like fluid, dissolves sulphur, iodoform, camphor, metal-salts, &c., and is itself soluble in water, benzin, carbon disulphide, ether, and chloroform.

## Sulphuric Acid

When sulphone (fig. 1029, p. 289) is joined by two hydroxyls, one on each side, we have sulphuric acid.

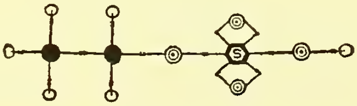
Fig. 1055



Sulphuric acid, $SH_2O_4$; b.p 338°

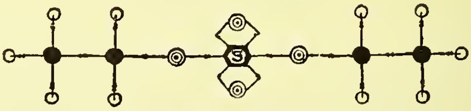
The chief part it plays in organic chemistry, as regards structures, is as one of the components in neutral, and acid compound ethers, combining with alcohols and phenols by separating one or two molecules of water. Thus with *ethyl-alcohol* it forms

Fig. 1056



Ethyl-sulphuric acid, sulpho-vinic acid, $C_2H_6SO_4$; syrupy fluid; decomposes on heating; the sodium salt is used as a cathartic

Fig. 1057



Ethyl-sulphate, $C_4H_{10}SO_4$; b.p. 208°

Ethyl-sulphuric acid is formed when alcohol and sulphuric acid are heated together. Ethyl-sulphuric acid when heated with alcohol forms ethyl-ether and sulphuric acid:

Fig. 1058

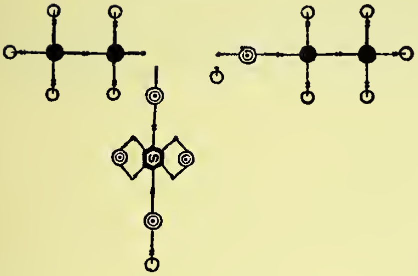
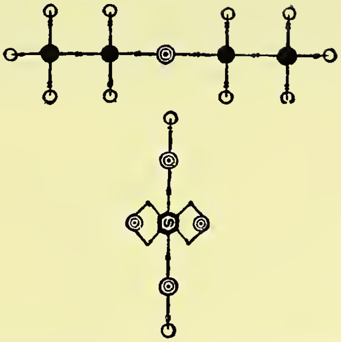


Fig. 1059



Ethyl-sulphuric acid and alcohol, one molecule of each = Ethyl-ether (*vide* fig. 473, p. 113) and sulphuric acid

The method of preparing ether, now upwards of 150 years old, is based upon this reaction. The molecule of sulphuric acid separated will form ethyl-sulphuric acid when a fresh molecule of alcohol is added, and will as such again form ether and sulphuric acid as long as fresh alcohol is added. In this way an unlimited quantity of alcohol would be transformed into ether by the same quantity of sulphuric acid but for the fact that the formation of ethyl-sulphuric acid is always accompanied by separation of one molecule of water.

Fig. 1060

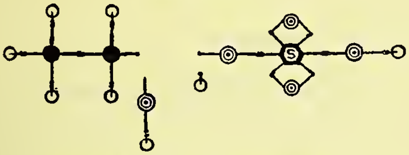
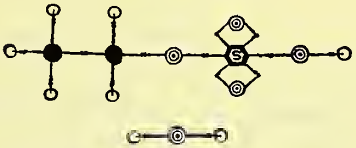


Fig. 1061

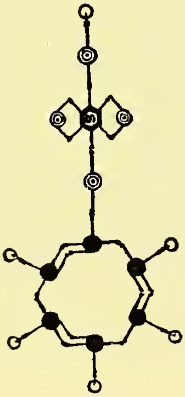


Ethyl-alcohol and sulphuric acid = Ethyl-sulphuric acid and water

The mixture becomes therefore at last so diluted that the sulphuric acid can form no more ethyl-sulphuric acid, which state will be accelerated by the fact that alcohol is never free from water; therefore water from this source also is constantly being added to the mixture.

Amongst the *phenyl-ethers* may be mentioned

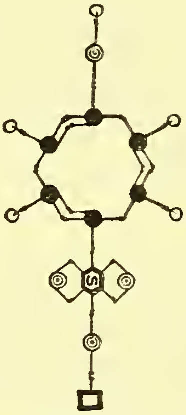
Fig. 1062



Phenyl-sulphuric acid, $C_6H_6SO_4$

The free acid decomposes almost immediately into phenol and sulphuric acid. The sodium-salt is used as an antiseptic for gonorrhœa. The potassium-salt is found in human urine; if it is heated to 150° it is by intramolecular change transformed entirely into potassium-*p*-phenol-sulphonate, the sulphonyl-part of the sulphuric acid exchanging places with the hydrogen in para-position.

Fig. 1063



Potassium-*p*-phenol-sulphonate (*vide* fig. 1046, p. 292)

## Future Nomenclature of Sulphur-compounds

Mercaptans receive the name of *thiols*; thio-ethers or sulphides form their names, in analogy to ethers, by placing *thio*, or in case of disulphides *dithio*, between the names of the hydrocarbons. Thio-aldehydes and thio-ketones become *thials* and *thiones*, and acids have their names formed, according as sulphur substitutes the singly or doubly bound oxygen, by the suffixes *thiolic acid* and *thionic acid*; when both oxygens have been substituted they receive the suffix *thion-thiolic acid*. Sulphones have *sulphone* placed between the names of the hydrocarbons.

| *Old Nomenclature* | | | *New Nomenclature* |
|---|---|---|---|
| Methyl-mercaptan | (fig. 991, p. 281) | = | Methane-thiol |
| Ethyl-mercaptan | (fig. 992, p. ,, ) | = | Ethane-thiol |
| Ethyl-sulphide | (fig. 994, p. ,, ) | = | Ethane-thio-ethane |
| Ethyl-disulphide | (fig. 996, p. ,, ) | = | Ethane-di-thio-ethane |
| Thialdehyde | (fig. 997, p. 282) | = | Ethane-thial |
| Thioxy-carbonic acid | (fig. 1000, p. ,, ) | = | Methane-thiolic acid |
| Di-thioxy-carbonic acid | (fig. 1001, p. ,, ) | = | Methane-di-thiolic acid |
| Tri-thio-carbonic acid | (fig. 1002, p. ,, ) | = | Methane-thion-di-thiolic acid |
| Oxy-di-thio-carbonic acid | (fig. 1003, p. 283) | = | Methane-thion-thiolic acid |
| Di-oxy-thio-carbonic acid | (fig. 1004, p. ,, ) | = | Methane-thion-di(oïc) acid |
| Di-methyl-sulphone | (fig. 1030, p. 289) | = | Methane-sulphone-methane |
| Sulphonal | (fig. 1036, p. 290) | = | Propane-2 : 2 di-sulphone-ethane |

The other classes of sulphur-compounds are not mentioned, and their nomenclature can scarcely be formed from the above rules.

# PART X.

# Nitrogen Compounds

# Nitrogen Compounds

Fig. 1064

*Index,* *Chemical symbol,* N

The next element with which to form new compounds is nitrogen, and the variety which this element is capable of producing is nearly inexhaustible.

Like sulphur, its valencies are varying in number, but unlike that element, the valencies of which were always even numbers, six, four, or two, those of nitrogen are always an uneven number, five, three, and perhaps one. It can combine equally well with electro-positive and electro-negative bodies, forming very strong bases or acids, and can replace carbon-atoms in closed chains.

We shall first mention the combinations of

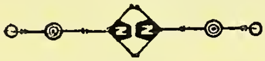
## NITROGEN AND OXYGEN

of which there are several; but only those with either one, two, or three atoms of oxygen are of importance in organic chemistry, forming acids when hydrogen enters into the radical.

## Hypo-nitrous Acid

The first of the oxygen-combinations, that with one atom of oxygen, *hypo-nitrous acid,* is probably a double molecule.

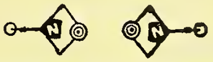
Fig. 1065



Hypo-nitrous acid, $N_2O_2H_2$; decomposes on being isolated

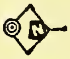
It forms salts and ethers. Only one of the latter (*di-azo-ethoxane*) is known so far. Joining other compounds, where only one valency is offered for its accommodation, it seems able to split up into *two molecules,* it conforming to circumstances by a re-arrangement of its structure:

Fig. 1066



of which the radical is

Fig. 1067



Two molecules of hypo-nitrous acid

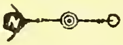
Nitrosyl

Thus, dropping a hydrogen-atom enables it to enter into direct union with a carbon-atom in benzene-compounds with one free valency (aliphatic combinations of this sort are exceptional).

These compounds are styled *nitroso-compounds* to distinguish them from the *oximes*, which may also be looked upon as formed from hypo-nitrous acid in the following way :

When two valencies of a carbon-atom are available, the double molecule of hypo-nitrous acid simply divides itself into two di-valent radicals :

FIG. 1068



Hydroximide, NOH

the two free valencies joining the carbon-atom's valencies. These compounds are termed **oximes** (contracted from hydroximide or oximide). As the formation of them in this way is purely theoretical they will presently be considered a little more fully under Nitrous Acid and Hydroxylamine.

## Nitrous Acid

The next combination is one atom of nitrogen and two of oxygen. Like the previous acid, and like sulphurous acid (p. 288), it seems capable of arranging itself into two structural forms, in one appearing as a triad, in the other as a pentad.

FIG. 1069

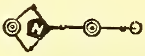
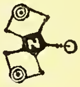


FIG. 1070



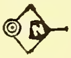
Nitrous acid, $NO_2H$; decomposes easily when slightly warmed

Salts of this acid are formed by metal replacing the hydrogen, just in the usual way. But all metals do not assert their influence upon the acid radical in the same degree ; some, *e.g.* alkali metals, are quite content to come into contact with the nitrogen, through the intervention of the oxygen, by replacing the hydrogen-atom of hydroxyl (fig. 1069, above) ; but this does not satisfy the noble silver ; it wants to come so near the nitrogen as to actually shake hands, and the acid has to comply by arranging things a little differently (fig. 1070, above). Therefore derivatives of the acid with such a structure, as in the silver-salts, are different from those of alkali salts.

We shall study the latter a little first.

As will be seen, we can make two radicals out of the nitrous acid, 1, *by removing the hydroxyl*:

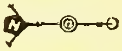
FIG. 1071



Nitrosyl, NO

when we have a mono-valent radical the substitution-products of which are the same *nitroso-compounds* as produced from *hypo-nitrous acid* (p. 301) ; and 2, *by removing the doubly-bound oxygen* :

FIG. 1072



Hydroximide, NOH

when we have a di-valent radical whose substitution-products are **oximes** (sometimes also termed iso-nitroso-compounds) mentioned above.

As said before, we have not succeeded in combining nitrosyl with any aliphatic compound, except in one or two cases to be subsequently (pp. 305 and 335) mentioned, but we know several aromatic nitroso-compounds with nitrosyl as substituent, either in the benzene- or in the aliphatic-part of the substance, but none of them is of sufficient interest for our purpose.

Oximes form a large series of compounds, but the greater part of them is the product of the action of hydroxylamine (a compound we are coming to, p. 380) upon aldehydes and ketones. As an example of oximes formed by nitrous acid we may mention iso-nitroso-acetone:

Fig. 1073

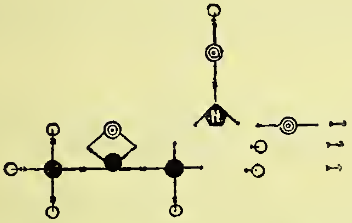


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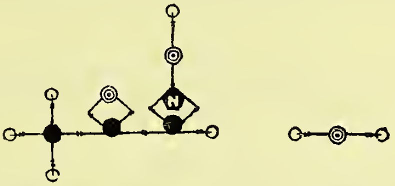
Fig. 1074



Acetone + nitrous acid = Iso-nitroso-acetone + Water
(*vide* fig. 566, p. 138) $C_3H_5NO_2$; m.p. 65°

Nitrous acid will with alcohols form compound-ethers when it has the structure we are now discussing. For instance:

Fig. 1075

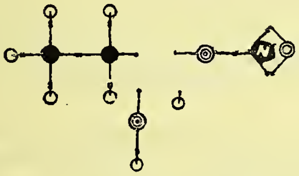


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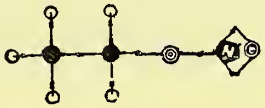
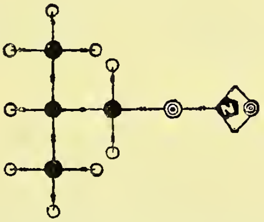
Fig. 1076



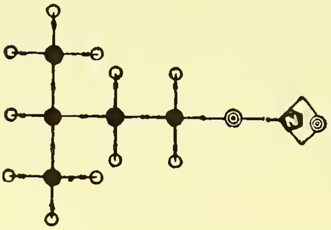
Alcohol + nitrous acid = Ethyl-nitrite, sweet spirits of wine, saltpetre-ether, $C_2H_5NO_2$; b.p. 18°; spiritus ætheris nitrosi is its alcoholic solution mixed with some by-products from its preparation, such as aldehyde &c.; a mild irritant

Fig. 1077



Iso-butyl-nitrite, $C_4H_9NO_2$; b.p. 67°; used for inhalation in asthma, angina pectoris, &c. Four isomers are known

Fig. 1078



Iso-amyl-nitrite (amyl-nitris, *Ph. B.*), $C_5H_{11}NO_2$; b.p. 94–99°; produces an expansion of the blood-vessels and a diminution of the controlling power of the contractile muscles; very poisonous; is employed internally and by inhalation in angina pectoris, asthma, epilepsy, &c.

The amyl-alcohol from which it is prepared does not, as a rule, consist entirely of the pure iso-compound; therefore *amyl nitris* is, as a consequence, slightly mixed with some of the isomeric amyl-nitrites.

Nitrous acid of the structure (fig. 1070, p. 302), which it has in the silver-salt, forms another series of compounds differing from the preceding ones by not being compound ethers: they are distinguished as nitro-compounds, and the radical of nitrous acid in this form is termed nitro-group. Thus from *methyl-alcohol* is formed

Fig. 1079

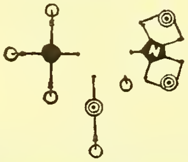
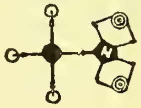


Fig. 1080



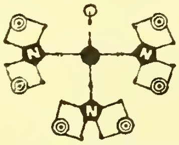
Methyl alcohol + nitrous acid = Nitro-methane, nitro-carbol, $CH_3NO_2$; b.p. 101°; the salts are explosive

The alcohols and the acid are practically not employed for preparing these compounds; methyl iodide (fig. 948, p. 265) and silver nitrite are used for the purpose. In these compounds iodine replaces the hydroxyl in the alcohol, and silver the hydrogen in the acid, the process going on as illustrated above, only that silver-iodide is separated instead of water.

For the sake of our theory, mention should not be omitted of the fact that this process is only carried out thoroughly by methane. The higher homologues deliver, besides nitro-compounds, also the compound-ethers; and the higher the homologue the more of the latter. A satisfactory explanation of this fact is still wanting.

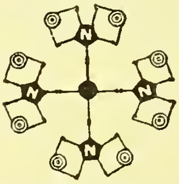
The nitro-group can also substitute the other hydrogen-atoms in the methane group; for instance:

Fig. 1081



Tri-nitro-methane, nitroform, $CHN_3O_6$; m.p. 15°; explosive

Fig. 1082

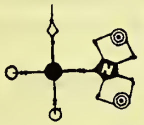


Tetra nitro-methane, nitro-carbon, $CN_4O_8$; m.p. 13°; b.p. 126°

The nitro-group imparts such an electro-negative character to the carbon-group as to make it a strong acid as long as there are hydrogen-atoms attached to the same carbon-atom. Such hydrogen-atoms, or at least two of them, are therefore replaceable by metals, forming salts. If all the hydrogen-atoms are replaced by nitro-groups the compound loses its acid character and becomes neutral. Thus nitro-, di-, and tri-nitro-methane are strong acids, but tetra-nitro-methane is neutral.

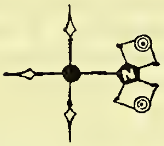
It is the same if some of the hydrogen-atoms are replaced by halogens. Although the hydrocarbon is made electro-negative by the presence of the nitro-group, it does not for that reason object to its remaining hydrogens being replaced by such electro-negative elements as the halogens; thus we have

Fig. 1083



Bromo-nitro-methane, $CH_2BNO_2$; b.p. 143°; a strong acid

Fig. 1084

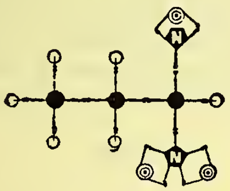


Tri-chloro-nitro-methane, chloropicrin, nitro-chloroform, $CCl_3NO_2$; b.p. 112°; neutral compound

Similar compounds have been prepared from some of the higher homologues of methane.

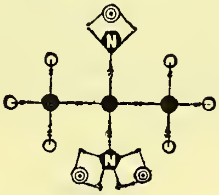
It is into these nitro-compounds that the radical nitrosyl has been successfully introduced; no other compounds of the aliphatic series have been found willing to combine with that radical, as mentioned p. 303. It attaches itself to the same carbon-atom that holds the nitro-group, and the ensuing products are termed nitrolic acids when both are combined with the methyl-group of an alcohol radical (primary alcohols), but when combined with a methylene-link (secondary alcohols) they are neutral bodies for the reason stated above, and are called pseudo-nitrols. The derivatives from propane or propyl-alcohol and iso-propyl-alcohol (figs. 338 and 339, p. 70) will serve to make this better understood:

Fig. 1085



Propyl-nitrolic-acid, $C_3H_6N_2O_3$; m.p. 60; an acid, because it *has* a hydrogen-atom connected with the same carbon-atom as the nitro- and nitrosyl-groups

Fig. 1086

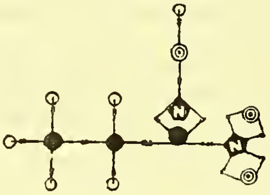


Propyl-pseudo-nitrol, $C_3H_6N_2O_3$; m.p. 76°; (decomp.) a neutral body, because *no* hydrogen-atom is connected with the same carbon-atom as the nitro- and nitrosyl-groups

The solutions of the nitrolic salts have a dark red colour, whereas the solutions of pseudo-nitrols are dark blue. This reaction is taken advantage of to determine whether an alcohol is primary, secondary, or tertiary, as nitrolic compounds are derived from primary, and pseudo-nitrols from secondary alcohols. Tertiary alcohols cannot form these derivatives, as they have no spare room for the nitrosyl (*vide* fig. 335, p. 69), and consequently give no colour-reaction in this way (*Liebermann's reaction*).

Some chemists are of opinion that the nitrolic acid has in its structure *hydroximide* (fig. 1068, p. 302) instead of *nitrosyl*; consequently propyl-nitrolic acid would have this structure:

Fig. 1087



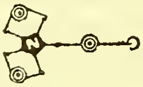
Propyl-pseudo-nitrol cannot have hydroximide in its structure, as there are not sufficient valencies and no hydrogen available. It seems more reasonable to give these two compounds analogous constructions; the nitrosyl-structure is perhaps, therefore, preferable.

There are a great many more nitro-compounds which may be theoretically derived from nitrous acid in a similar way; but as all of them can theoretically be equally well derived, and practically are derived, from nitric acid, they will be mentioned under that head.

## Nitric Acid

Nitrogen is penta-valent in nitric acid, uniting with three atoms of oxygen, one of which forms hydroxyl with a hydrogen-atom; consequently its structure may be thus depicted:

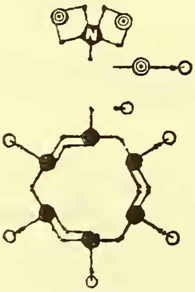
Fig. 1088



Nitric acid, $NHO_3$; b.p. 86°

Nitric acid does not readily form nitro-compounds direct from the single-linked hydrocarbons of the aliphatic series; a couple or so, formed from hydrocarbons, with double bonds appear to be known, and a few secondary nitro-compounds have recently been prepared from the normal saturated hydrocarbons (*Ber.* xxv. *Ref.* p. 108; see also xxvi. p. 129), else it has ordinarily no action upon them. The aromatic hydrocarbons, however, and their derivatives are easily reacted upon by nitric acid, their hydrogen-atoms forming water with the acid's hydroxyl, and the nitro-group taking the place of the hydrogen:

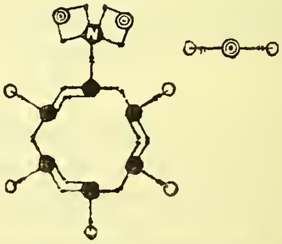
Fig. 1089



Benzene and nitric acid

=

Fig. 1090

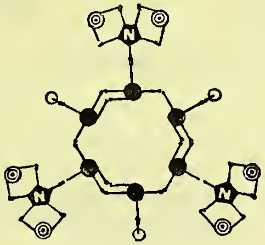


Nitro-benzene, essence of mirban, artificial bitter-almond oil, $C_6H_5NO_2$; b.p. 210°

Nitro-benzene is used in large quantities for the manufacture of colours, also in perfumery, on account of its odour being very like that of bitter-almond-oil (*vide* fig. 554, p. 134). Poisonous.

As many as three, but not more, nitro-groups have been thus introduced into benzene and its derivatives.

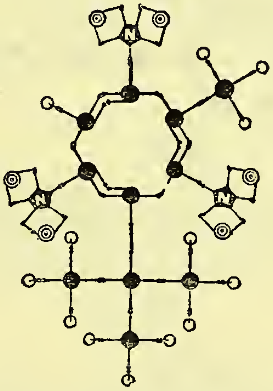
Fig. 1091



Symmetrical tri-nitro-benzene, $C_6H_3N_3O_6$; m.p. 121°

When an iso-butyl (fig. 53, p. 13, also Table, p. 82) is placed in para-position to one of the nitro-groups and methyl in ortho-position, we obtain a compound with a strong musk-like odour.

Fig. 1092

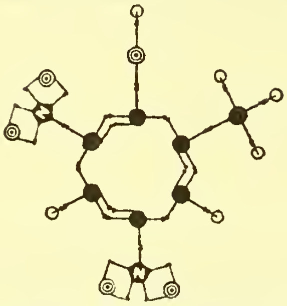


Tonquinol, artificial musk, tri-nitro-butyl-toluol, $C_{11}H_{13}N_3O_6$; m.p. 96°; the commercial product is a mixture of 10 per cent. of this compound and 90 per cent. of acetanilide

Though tonquinol is only two or three years old it has already found a rival, which can do things better, can dissolve itself in water, which tonquinol can not. This opposition-compound consists of a benzene-ring in which the hydrogen-atoms are replaced by 1, two methyls (*xylene*, p. 44); 2, one iso-butyl; 3, a sulphonyl (fig. 1037, p. 290); and 4, a nitro-group. The different positions of these radicals in the benzene-ring have not been ascertained: its systematical name would be *nitro-sulpho-iso-butyl-xylene*; it does not appear to have received a trade name yet (*Ph. C.* xxxiii. p. 80).

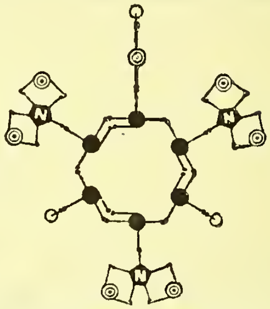
Of nitro-compounds from other benzene-derivatives we shall call attention to two:

Fig. 1093



*o*-Di-nitro-cresol, $C_7H_6N_2O_5$; explosive crystals; m.p. 85°

Fig. 1094



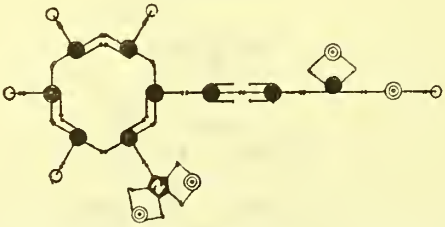
Picric acid, tri-nitro-phenol, $C_6H_3N_3O_7$; yellow crystals; m.p. 122°·5; a yellow dye; explosive; the chief constituent in the French explosive *melinite*

The potassium salt of the *o*-di-nitrol-cresol (the metal replaces hydrogen in hydroxyl) is an excellent insect-killer, and mixed with equal parts of soap is, under the name of antinonnine, used for freeing plants from all sorts of noxious insects, wood from dry-rot (*Merulius polyporus*, *trametes*, &c.), and for killing rats and mice.

Also in scabies it is said to be an effective remedy.

From *phenyl propiolic acid* (fig. 822, p. 215) we have an ortho-nitro-compound:

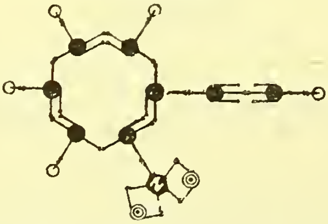
Fig. 1095



Ortho-nitro-phenyl-propiolic acid, $C_9H_5NO_4$; crystals, decomp. at 155°

Boiled with water this acid looses its carboxyl, and is turned into a hydrocarbon:

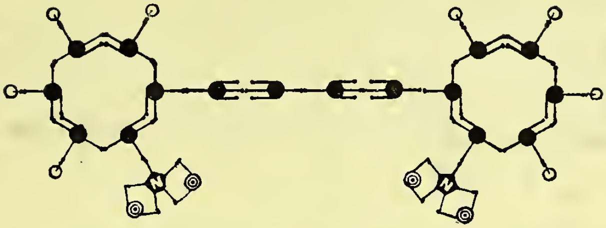
Fig. 1096



Ortho-nitro-phenyl-acetylene, $C_8H_5NO_2$; m.p. 81°; compare fig. 291, p. 55

Through copper, which is a dyad, two molecules of the above hydrocarbon are joined, the copper replacing the hydrogen in each of the two acetylenes; and then eliminating the copper by oxidation we get the two nitro-phenyl-acetylenes directly united:

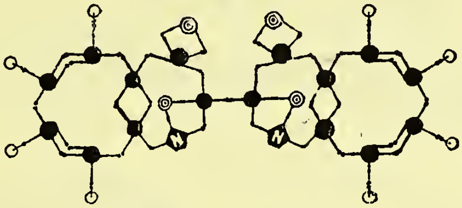
FIG. 1097



Di-nitro-di-phenyl-di-acetylene, $C_{16}H_8N_2O_4$; m.p. 212°

When this compound is treated with sulphuric acid an intramolecular change takes place without elimination of anything. The re-arrangement concerns only the nitro- and acetylene-groups; one oxygen goes to one of acetylene's carbons, breaking the triple bond, turning it into a single one, and taking possession of the two valencies thus set free; the other oxygen sticks with one valency to the nitrogen and unites through the second valency with one of the other carbon's free valencies liberated by breaking the triple bond. There are now four free valencies left, three of which belong to the nitrogen and one to the second carbon. This last one unites with one of nitrogen's free valencies forming a closed chain (pentagon), and the two remaining free valencies of the nitrogen disappear, the pentad being reduced to a triad.

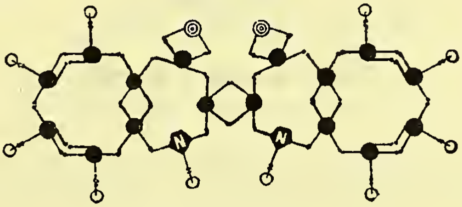
FIG. 1098



Di-isatogen, $C_{16}H_8N_2O_4$

When, again, di-isatogen is treated with reducing agents, the oxygens inside the pentagons are withdrawn; two valencies thus set free unite the two isatogen-groups by a double bond, and the free nitrogen-valencies are each provided with a hydrogen from the reducing agent:

FIG. 1099



Indigo, $C_{16}H_{10}N_2O_2$

**Indigo** is obtained from several plants, but especially from *Indigofera tinctoria,* in which it is present in reduced state (indigo-white, fig. 1295, p. 365) as a glucoside.

In its quality of an acid, nitric acid forms compound ethers with alcohols. Some of these are

Fig. 1100

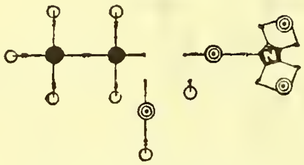
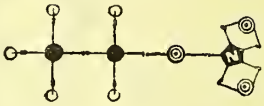


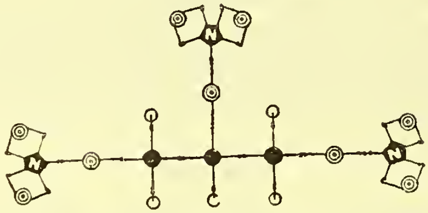
Fig. 1101



Alcohol and nitric acid = Ethyl nitrate, $C_2H_5NO_3$ ; b.p. 86°·3 ; explosive fluid

From *glycerin* and *nitric acid*:

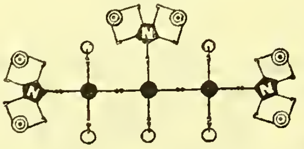
Fig. 1102



Nitro-glycerin, glycerin nitrate, trinitrin, glonoïn, angio-neurosine, $C_3H_5N_3O_9$ ; an oily fluid, explodes on heating; poisonous; used in neuralgia, migraine, asthma, &c.; a mixture of nitro-glycerin and silicious earth (*Silex farinaceus*, Kieselguhr) is called dynamite

As nitro-glycerin is a compound ether in which nitro-groups are joined to the carbon-atoms through an oxygen-atom by replacing hydrogen in hydroxyl, this name is scientifically not the proper designation. In nitro-compounds the nitro-groups are joined directly to the carbon-atoms, and not through the intervention of oxygen, because they displace the whole hydroxyl, and not its hydrogen only, as in the compound ether above. They are therefore identical with the corresponding nitro-hydrocarbons. The true nitro-glycerin is thus the same as tri-nitro-propane, and has the following structure:

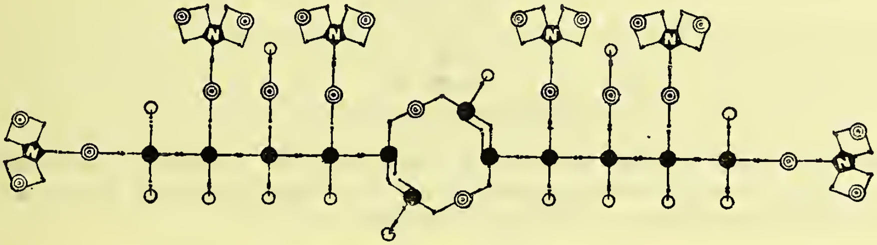
Fig. 1103



True nitro-glycerin or tri-nitro-propane, $C_3H_5N_3O_6$ ; oily fluid; b.p. 200°; the hydrogens other than the hydroxyls' in alcohols cannot be replaced by nitro-groups

From carbohydrates (p. 151), which it will be remembered are alcohol-aldehydes and alcohol-ketones, some important compound ethers are formed with nitric acid. The most noted amongst them are the cellulose compounds (*vide* p. 158). We do not know the structure of cellulose; the only thing we can conclude from its chemical behaviour is that it must be a combination of several molecules of hexoses by elimination of water, and that its empirical formula is $(C_6H_{10}O_5)x$, where $x$ stands for an unknown figure, which for the sake of illustration we will take to be equal to 2. We will further, for the same reason, suppose, quite arbitrarily—for we know nothing about it—that the two molecules are joined somewhat in lactide fashion (*vide* fig. 935, p. 257). Into this double molecule it is possible to introduce by way of etherification, from two to six, radicals of nitric acid. The hexa-nitrated ether would thus have some such structure:

Fig. 1104



Cellulose hexa-nitrate, $C_{12}H_{14}N_6O_{22}$

Other names are gun-cotton, pyroxylin, and, quite improperly (see above), nitro-cellulose. It is insoluble in a mixture of alcohol and ether.

The chief constituent of the different sorts of so-called smokeless gunpowder is pyroxylin, prepared from various cellulose-sources (*e.g.* straw) mixed with other things, such as camphor, potassium-nitrate and -chlorate, barium-nitrate, &c., which either modify or increase its explosive property. The new smokeless powder, cordite, consists of gun-cotton dissolved in acetone and nitro-glycerin, being afterwards formed into strings or cubes. Celluloid is a mixture of pyroxylin and camphor. When nitrated cellulose is subjected to reducing agents the nitric radicals are removed and the pure cellulose is restored. Textile fabrics treated in this manner are said to become much stronger, and are disliked by moths and other insects. Such fabrics are known by the name of pilou. Compressed pyroxylin is used for torpedoes.

Cellulose penta- and tetra-nitrate are soluble in a mixture of alcohol and ether, and used for the preparation of collodium; hence they are distinguished as colloxylins. Mixed with nitro-glycerin they form a gelatinous mass used for blasting purposes. Ballistite is the name of one of these compounds. Zapon is the name of colloxylins dissolved in amyl-acetate and amyl-alcohol; camphoïde, if they are dissolved with camphor in absolute alcohol; and crystalline when dissolved in methyl-alcohol.

## Future Nomenclature of Organic Compounds' Union with Combinations of Nitrogen and Oxygen

The only two Congress rules referring to these compounds are—

1. *Iso-nitroso-compounds will be considered and named oximes.* Therefore they will be mentioned under that heading, p. 320.
2. *Nitro-compounds retain throughout their present designation.*

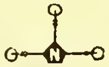
As the nomenclature of cyclo-compounds has not yet been settled, and as interpreters of the rules do not agree on the nomenclature of poly-valent radicals, it is impossible to give examples from the preceding pages except that of true nitro-glycerin (fig. 1103, p. 310), which will receive the name of 1 : 2 : 3 nitro-propane.

# NITROGEN AND HYDROGEN

## Ammonia and Ammonium

Nitrogen combines as a triad with hydrogen, forming ammonia :

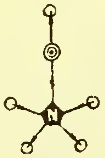
Fig. 1105



Ammonia, $NH_3$; a gas; b.p. −40°

Like the behaviour of sulphur's valencies (p. 286), two more valencies in ammonia's nitrogen may come into play when an electro-negative group or element is affixed to one of them; for instance, hydroxyl, chlorine, bromine, iodine, acid-radicals, &c.:

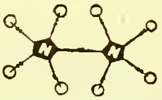
Fig. 1106



Ammonium hydroxide, $NH_5O$

It is supposed to be existing in the solution of ammonia in water, but has not been isolated, nor has ammonium itself, which probably would consist of two ammonium radicals joined.

Fig. 1107



Ammonium, $N_2H_8$

It is very much like a metal in its chemical properties, but should it ever be obtained in free state it would probably prove to be a gas.

These two compounds can combine in a most varied manner with other organic compounds, forming perhaps the largest and one of the most important sections of organic chemistry, including the alkaloïds, the greater part of the modern synthetical remedies, and dyes. The study of this subject may be considered scarcely out of its 'teens' yet, but is in a state of very promising development, growing so quickly that its most intimate friends would hardly recognise it after but a few years' absence.

The process of combination takes place *partly* by the hydrogen-atom in the two compounds being replaced by other compounds, or even by one or more of their own kin, and *partly* by these two compounds, or their derivatives, replacing hydrogens in other compounds, although, of course, in some cases where two compounds only unite there is no distinction between the two processes.

We may thus divide them into two large classes with subdivisions; in the following classification, however, this is not adhered to, as thereby nearly allied compounds would sometimes be widely separated, and their relationship would be lost sight of.

A short description of the structural forms of the several classes will precede the derivatives of such members of each class as are supposed to have sufficient interest for us.

# Ammonia's Combinations with Hydrocarbons Amines (Amido-compounds)

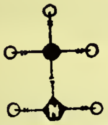
## MONAMINES

### Primary Ammonia-bases

(AMIDO-BASES)

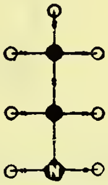
If only one hydrogen-atom in ammonia is substituted by a radical we obtain what is termed an amido-compound; if the radical is from the aliphatic series they are commonly distinguished as amines; in cyclo-compounds it depends upon how we regard them; if we look upon them as cyclo-compounds in which ammonia has been introduced we call them amido-compounds; but if we consider them ammonia in which cyclo-compounds have been introduced they also are termed amines.

Fig. 1108



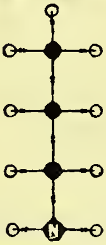
Methylamine, $CH_5N$; a gas

Fig. 1109



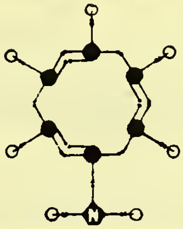
Ethylamine, $C_2H_7N$; b.p. 18°·7

Fig. 1110



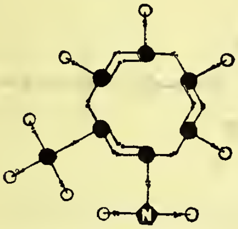
Propylamine, $C_3H_9N$; b.p. 44°

Fig. 1111



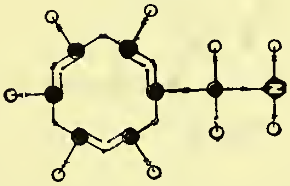
Amido-benzene or phenylamine, aniline, $C_6H_7N$; b.p. 184°

Fig. 1112



*o*-Toluidine, $C_7H_9N$; b.p. 197°

Fig. 1113



Benzylamine, $C_7H_9N$; b.p. 183°

Methylamine occurs in a plant, *Mercurialis annua* and *perennis*, in herring brine, and in crude wood-spirit. Water absorbs more of this gas than of any other (1150 volumes at 12°·5).

Ethylamine is a stronger base than ammonia.

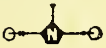
Propylamine is used in chorea and rheumatism; is formed by the putrefaction of glue.

Aniline, poisonous, has been used as a destroyer of lupus nodules. It is now manufactured on a large scale from nitro-benzene (*vide* p. 335), originating in the first instance from coal-tar. It is chiefly used in the colour industry.

Bromamide, a new American anti-neuralgic, is said (*Amer. Journ. Pharm.*; *Ph. C.* xxxiv. p. 100) to be aniline, in which three benzene- and one amido-hydrogens are replaced by bromine.

*o*-Toluidine occurs together with para- and meta-compounds in coal-tar.

Fig. 1114

That part of ammonia which remains unaltered, $NH_2$  is termed an amido-group.

(For further development see p. 341.)

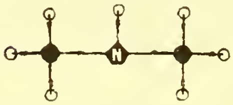
## Secondary Ammonia-bases

### (IMIDO-BASES)

When two of the hydrogen-atoms in ammonia are replaced by hydrocarbon-radicals the compounds are termed secondary- or imido-bases, the rest of ammonia in which only one of the hydrogens is left undisturbed being designated as an imido-group, NH. Their nomenclature is formed by placing 'di-' before the hydrocarbon radical, indicating that there are two of them in the compound.

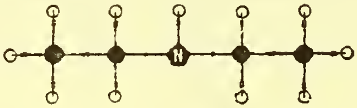
Thus we have

Fig. 1115



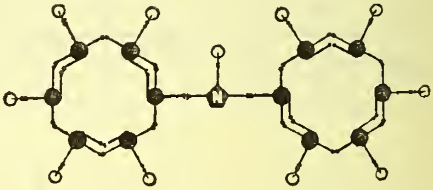
Di-methylamine, $C_2H_7N$ ; b.p. 8° ; present in herring-brine and sausages ; not poisonous

Fig. 1116



Di-ethylamine, $C_4H_{11}N$ ; b.p. 57°

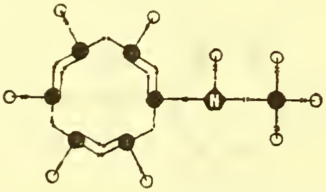
Fig. 1117



Di-phenylamine, $C_{12}H_{11}N$ ; m.p. 54° ; derivatives form dyes (*aurantia* and di-phenylamine-blue)

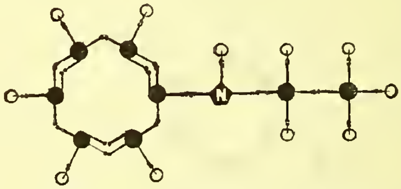
The substituting groups need not be of the same sort; they may be varied according to taste; for instance :

Fig. 1118



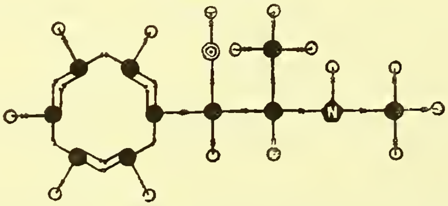
Methyl-aniline, $C_7H_9N$ ; b.p. 191°

Fig. 1119



Ethyl-aniline, $C_8H_{11}N$ ; b.p. 204°

Fig. 1120



Pseudo-ephedrine, phenyl-hydroxy-propyl-methylamine, $C_{10}H_{15}NO$ ; m.p. 114° (Heger, *Neue Arzneimittel*, 1891) ; a new mydriatic remedy, said to be ever so much better than any other.

(For further development see p. 351.)

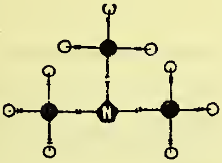
## Tertiary Ammonia-bases

(NITRILE-BASES)

When all three hydrogen-atoms in ammonia are replaced we obtain tertiary bases. The rest of ammonia consists, then, of an atom of the triad nitrogen, which may be considered the radical of tertiary bases, and is also distinguished as such by German chemists as nitrile, and its derivatives of this class as nitrile-bases, but it has not been generally adopted by English-speaking chemists, the name being reserved for another series of compounds, the cyanides of alcohol-radicals, where the three valencies are linked to one carbon-atom (*vide* p. 419).

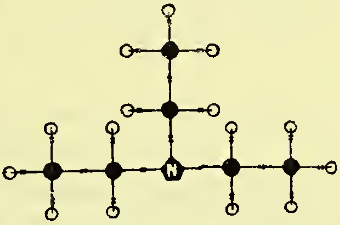
Analogous to secondary bases, the nomenclature is formed by placing 'tri-' before the hydrocarbon-radical.

Fig. 1121



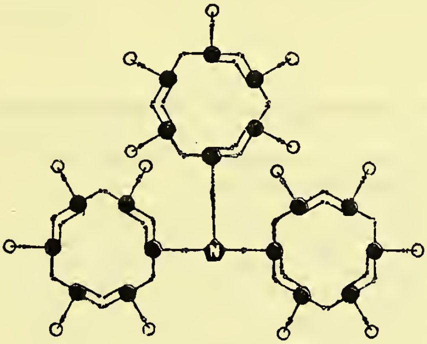
Tri-methylamine, $C_3H_9N$; b.p. variously stated from 3°·2–9°·5; occurs in herring-brine; was mistaken for propylamine in earlier chemical works; it is used in chorea minor, articular and acute rheumatism, and *paralysis agitans*

Fig. 1122



Tri-ethylamine, $C_6H_{15}N$; b.p. 91°; is a product of putrefying fish; not poisonous

Fig. 1123



Tri-phenylamine, $C_{18}H_{15}N$; m.p. 127°

(For further development see p. 353.)

## Future Nomenclature of Ammonia-bases

In the combinations of ammonia with hydrocarbons the latter are to be considered substituents, and the compounds to be distinguished as *amines* and not as amido-, imido-, or nitrile-bases.

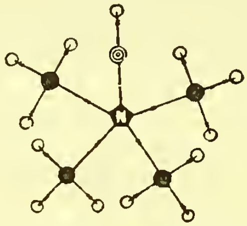
Methyl-, ethyl-, propyl-, di-methyl, di-ethyl-, tri-methyl-, ethyl-methyl-, &c., amines retain, therefore, their respective names.

## Quarternary Bases

(AMMONIUM-BASES)

As previously stated, the triad ammonia turns into a pentad when it comes into contact with electro-negative compounds. Substituted ammonias behave in an analogous manner, the electro-positive part of such compounds going to one valency and the rest to the other. The word 'tetra-' is placed before the name of the compound (provided, of course, that the substituting groups are of the same sort) and that of the electro-negative part after; *e.g.*

FIG. 1124



Tetra-methyl-ammonium-hydroxide, $C_4H_{13}NO$; a crystalline mass; decomposes on heating; used as an antiseptic in diphtheria

A corresponding phenyl compound does not exist. All alkyl compounds are strong bases, some even stronger than ammonia and as powerful as the fixed caustic alkalis which they greatly resemble in their chemical properties.

Phenyl-compounds of *ammonia*, on the other hand, are weak bases; the more phenyl they contain the more they lose of their basic character, so that tri-phenylamine is a neutral compound, and will not, therefore, be excited into a pentad in the presence of electro-negative bodies, nor will it form tetra-phenyl-ammonium-compounds.

(For further development see p. 354.)

## Future Nomenclature of Quarternary Bases

Nothing is said in the Congress resolutions of these bases except of one group, viz. *betaïnes* (*vide* p. 356), which is thus specially mentioned—

'*The suffix to distinguish this function is -taïne. Example: Ethanoyltrimethyltaïne.*'

The example is betaïne proper (fig. 1265, p. 355), in the structure of which there is a closed chain. Ethanoyl, however, the radical of acetic acid with its carboxyl unaffected (*vide* p. 202), is an open straight chain which would constitute the compound an acid; consequently the suffix *-taïne* must be intended to denote a closed chain in the structure, and the opportunity of using this suffix for all the substituted hydroxyl-ammonium compounds (*vide* fig. 1124, above) with choline, neurine, muscarine, &c., is thereby excluded.

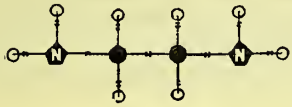
If the group $\equiv$ NOH had been designated by the suffix *-taïne* (hydroxyl-amone?) we would have had the means of providing all the quarternary bases besides the betaïne-like compound (including amido-acids) with names, though the use of *-taïne* for this purpose would scarcely be considered a very happy idea.

The ring-formation might be indicated by the prefix cyclo-, or described according to Professor Armstrong as tetra-phane (*Proceedings of the Ch. S.* 1892–93, No. 1134, and *Chemical News*, lxvi. p. 31).

## DIAMINES

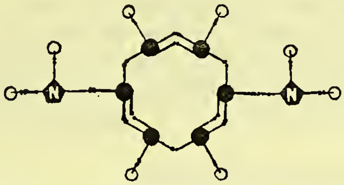
The former class was termed monamines because the compounds were formed by substitutions in one ammonia molecule. Diamines are so called because they are formed through substitutions by two ammonias in one or more hydrocarbons. As example may be illustrated

Fig. 1125



Ethylene-diamine, $C_2H_8N_2$; m.p. 10°; b.p. 116°·5

Fig. 1126



*p*-Diamido-benzene, *p*-phenylene diamine, $C_6H_8N_2$; m.p. 147°; photographic developer

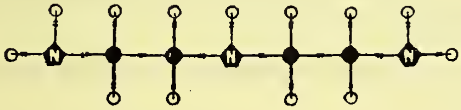
(For further development see p. 356.)

## POLYAMINES

Chemists have not succeeded in affixing more than two amido-groups to one aliphatic hydrocarbon-molecule, but as many as five amido-groups have been joined to cyclo-compounds.

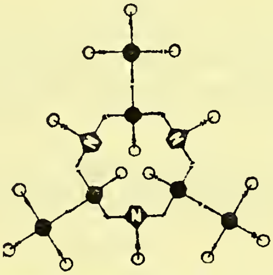
Two or more molecules of hydrocarbons can, however, be joined by three or more ammonia-rests: one or more will in this case be imido-groups because of having a hydrogen-atom on each side. When the number of ammonia-groups and hydrocarbon-groups are equal, they will form closed chains by dropping a hydrogen-atom from each end of the open chain. Amongst these compounds are such as

Fig. 1127



Di-ethylene triamine, $C_4H_{13}N_3$; b.p. 208°

Fig. 1128



Tri-ethylene-triamine, $C_6H_{15}N_3$; b.p. 216°

(For further development see p. 360.)

## Future Nomenclature of Diamines and Polyamines

The old method of constructing the nomenclature is adopted, subject, of course, to preceding rules. When, however, the group NH closes a chain it is termed *imine*.

| *Old Nomenclature* | | | *New Nomenclature* |
|---|---|---|---|
| Ethylene-diamine | (fig. 1125) | = | Ethane-diamine |
| Di-ethylene-triamine | (fig. 1127) | = | Di-ethaneamine-amine |
| Tri-ethylene-triamine | (fig. 1128) | = | Tri-ethane-triimine |

Both *Berichte* and *Agenda* have in the first example Ethene-diamine—why I know not.

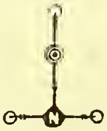
# Ammonia's Combinations with Hydroxyl

## HYDROXYLAMINE

We have seen that the triad nitrogen turns into a pentad when one of its valencies is joined to hydroxyl or another electro-negative body. This presupposes that an electro-positive body is at hand to take up the fifth valency. If not, ammonia will give up one of its hydrogens and offer the place to hydroxyl, forming a compound which has been termed hydroxylamine, and has been successfully isolated about a year ago (*Rec. Trav. chim.* x. p. 101); derivatives have been known some years.

The structure is therefore

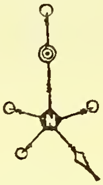
Fig. 1129



Hydroxylamine, hydroxy-ammonia, $NH_3O$; large crystals; m.p. 33

It is a base, and will take up by addition hydrochloric acid.

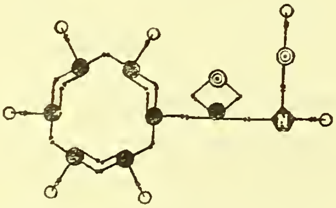
Fig. 1130



Hydroxylamine chloride, hydroxy-ammonium chloride, $NH_4ClO$; crystals; m.p. 100°; used in skin diseases as a substitute for pyrogallic acid, chrysarobin, &c.

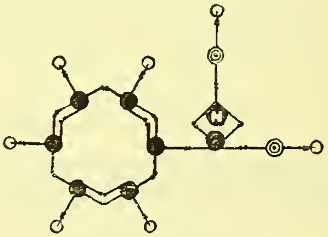
Hydroxylamine will also combine with benzoic acid, separating a molecule of water; two structures are possible and have been suggested.

Fig. 1131



Benz-hydroxylamine, $C_7H_7NO_2$; m.p. 124°

Fig. 1132



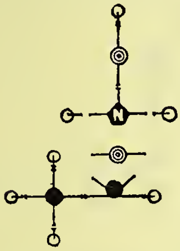
Benz-hydroxamic acid

The first is a substituted hydroxylamine, the second is a hydroxamic acid (see below), but which of the two is the right one has not yet been decided; researches and discussions are still going on—may be that both are right (molecular change).

All three hydrogen-atoms of hydroxylamine are replaceable by benzoyl; if one or two hydrogen-atoms are thus replaced the substitution-products behave like acids, and are therefore termed respectively hydroxamic and hydroximic acids; the compound with three hydrogens replaced is, however, a neutral compound.

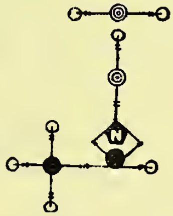
Hydroxylamine has a structure analogous to nitrous acid (fig. 1069, p. 302) with this difference, that two valencies in the latter bind an oxygen-atom, whereas they each have a hydrogen-atom in the former. On account of this similarity of structure they are capable of forming a series of the same sort of compounds, viz. oximes (*vide* p. 303) by separating a molecule of water; therefore nitrous acid with its oxygen will form them from compounds where *two hydrogens are bound to the same carbon-atom* (*vide* fig. 1073, p. 303), whereas hydroxylamine with its two hydrogens will form them from compounds in which *a carbon-atom is joined to an oxygen-atom* by two of its valencies (carbonyl): aldehydes and ketones are such compounds. The oximes from the former are termed aldoximes, from the latter ketoximes or simply oximes.

Fig. 1133



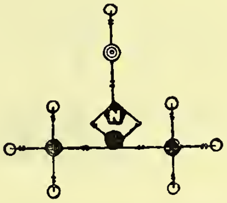
Aldehyde (fig. 538, p. 131) + hydroxylamine =

Fig. 1134



Acetaldoxime, $C_2H_5NO$; b.p. 114°

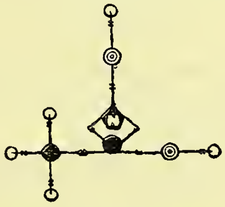
Fig. 1135



Acetoxime, $C_3H_7NO$; m.p. 60°; from acetone (fig. 566, p. 138)

Hydroxylamine has also been introduced into the carbonyl of acids in the same way as when it forms oximes. We have just had occasion to mention its combination with benzoic acid (fig. 1132, p. 318). An example from the fatty acids is

Fig. 1136

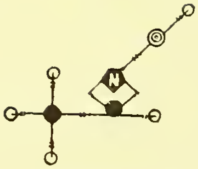


Aceto-hydroxamic acid, $C_2H_5NO_2$; m.p. 87° (*Ber.* xxii. p. 2854)

As a class they are distinguished as hydroxamic acids.

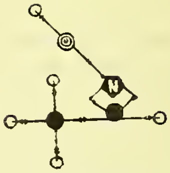
In many cases it has been found that hydroxylamines and analogous compounds (hydroxamic acids, hydrazones, p. 338 &c.) form isomers, which must be stereo-isomers. It has been suggested (*Ber.* xxv. p. 1908) that the hydroxyl in these cases does not stand, as it were, impartially (perpendicularly) between the groups on each side (they being different groups), but leaning over to one side or the other is thus supposed to influence these groups differently. In order to express this position with our symbols we have only to turn the nitrogen-symbol upside down:

Fig. 1137



Syn-acetaldoxime

Fig. 1138



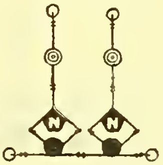
Anti-acetaldoxime

and in order to distinguish the isomers by names it has also been proposed to prefix the compound by *syn-* (syn-aldoximes) when the configuration is as in the first of the figures above, and by *anti-* (anti-aldoximes) when the hydroxyl leans the other way. The above structures are only geometrical expressions for nitrogen's stereo-isomerism.

Di-aldehydes and di-ketones form similar compounds with hydroxylamines.

From *Glyoxal* (fig. 545, p. 132):

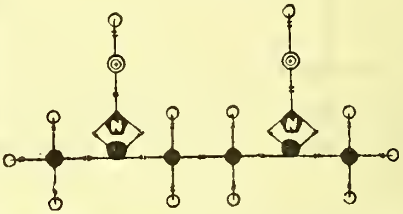
Fig. 1139



Glyoxime, $C_2H_4N_2O_2$; m.p. 178°

From *Acetonyl acetone* (fig. 578, p. 140):

Fig. 1140



Acetonyl-acetoxime, $C_6H_{12}N_2O_2$; m.p. 134°

## Future Nomenclature of Iso-nitroso-compounds, Hydroxylamines, and Oximes

The Congress rules affecting these bodies are—

1. Compounds derived from hydroxylamine by substitutions of the *hydroxylic* hydrogen retain the suffix *hydroxylamine.*

2. Oximes are to be distinguished by adding the word *oxime* to the hydrocarbon from which they are derived.

The first rule is simple enough, but we have had no occasion to mention any of these compounds on the preceding pages.

The second rule had the following rider added to it in the resolution published in *Nature* (omitted in *Agenda*, perhaps, because it is considered self-evident):

'Iso-nitroso-compounds are looked upon as *oximes*.'

The only, and also sufficient, way in which aldoximes can be distinguished from ketoximes in the new nomenclature is, therefore, by the numerals indicating the place of hydroxylamine.

| *Old Nomenclature* | | *New Nomenclature* |
|---|---|---|
| Iso-nitroso-acetone | (fig. 1074, p. 303) = | Propanone-oxime |
| Propyl-pseudo-nitrol | (fig. 1087, p. 306) = | 1 Nitro-propane-1 oxime |
| Acetaldoxime | (fig. 1134, p. 319) = | Ethane-oxime |
| Acetoxime | (fig. 1135, p. 319) = | Propane-2 oxime |
| Glyoxime | (fig. 1139, p. 320) = | Ethane-dioxime |
| Acetonyl-acetoxime | (fig. 1140, p. 320) = | Hexane-2 : 5 oxime |

and if also hydroxamic acids are to be considered derivatives from the corresponding hydrocarbons and not from the acids:

Aceto-hydroxamic acid (fig. 1136, p. 319) = Ethanol-1 oxime.

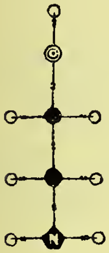
# Ammonia's Combinations with Alcohols

## HYDRAMINES

Hydrogen in ammonia may be displaced by radicals of mon-acid alcohols with elimination of two hydrogens or of poly-acid alcohols with elimination of water, such compounds being termed hydramines. According to the number of hydrogen-atoms thus or otherwise replaced, primary, secondary, and tertiary bases are obtained.

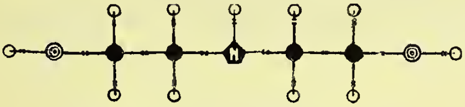
We know of substitutions by *ethyl-alcohol* (or *glycol*):

Fig. 1141



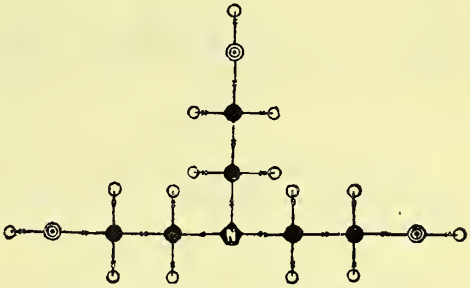
Hydroxy-ethylamine, ethoxyl-amine, $C_2H_7NO$ primary base

Fig. 1142



Di-ethoxyl-amine, imido-ethyl-alcohol, $C_4H_{11}NO_2$; secondary base

Fig. 1143



Tri-ethoxyl-amine, azo-ethyl-alcohol, $C_6H_{15}NO_3$; tertiary base

Syrupy liquids

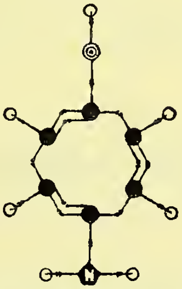
For tertiary bases retaining, on account of their hydroxyl, the properties both of a base and an alcohol, and their ability to form ethers of a basic character, a collective name, alkines, has been proposed, and for their ethers the name of alkeïnes (*Ber.* xix. p. 1873).[1]

# Ammonia's Combinations with Phenols

## AMIDO-PHENOLS

Phenol and ammonia combine in the same manner, that is, one to three ammonias may unite with one phenol, but not more than one phenol can join one ammonia, *e.g.*

Fig. 1144



*p*-Amido-phenol, $C_6H_7NO$; m.p. 184°; an excellent photographic developer; the ortho- and meta-compounds have also been prepared

(For further development see p. 346.)

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[1] Although the definition comprises tertiary bases only, the proposer of the name calls conhydrine (fig. 1430, p. 396) an 'alkine,' though it is not a tertiary but a secondary base. This class-name should therefore be used with a certain amount of reserve until a better definition turns up.

## Ammonia's Combination with Aldehyde

Ammonia can be added to acetic aldehyde (fig. 538, p. 131), causing a re-arrangement of its structure by giving up one of its hydrogen-atoms to aldehyde's oxygen, and assuming itself the place vacated by changing the double bond into a single one:

Fig. 1145

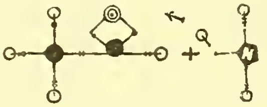
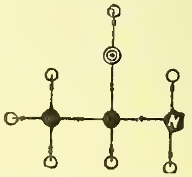


Fig. 1146



Aldehyde + ammonia = Aldehyde-ammonia, $C_2H_7NO$; m.p. 80°

When two molecules of sulphuretted hydrogen act upon three molecules of aldehyde ammonia, two molecules of ammonia and three of water are split off, and two atoms of sulphur take the place of ammonia:

Fig. 1147

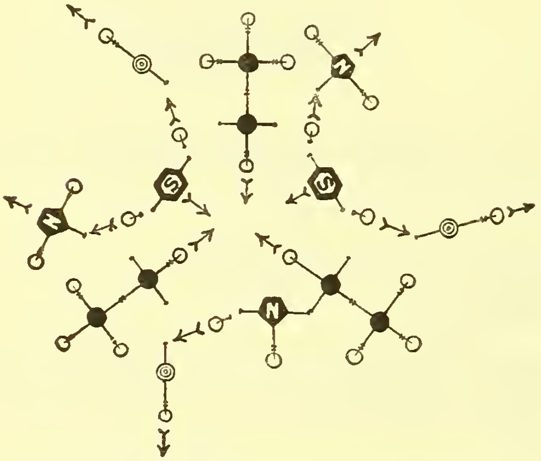
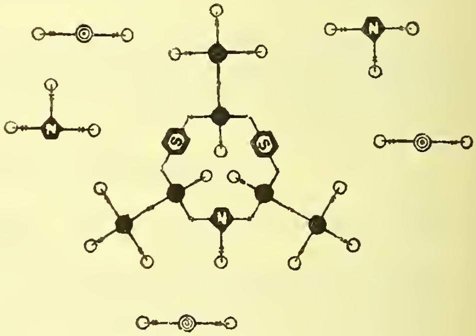


Fig. 1148



Three molecules of aldehyde ammonia + two molecules of sulphuretted hydrogen = Thialdine, $C_6H_{13}NS_2$; m.p. 43°; + three molecules of water and two molecules of ammonia; poisonous (*Medical Annual*, 1892)

(For derivative see p. 368.)

### Future Nomenclature of Hydramines and Aldehyde-ammonias

The rules already given are sufficient to form the names in these classes:

*Old Nomenclature* *New Nomenclature*

Hydroxy-ethyl-amine (fig. 1141, p. 321) = Ethane-2 ol-amine
Di-ethoxyl-amine (fig. 1142, p. 321) = Di-ethane-2 ol-amine
Tri-ethoxyl-amine (fig. 1143, p. 321) = Tri-ethane-2 ol-amine
Aldehyde-ammonia (fig. 1146, p. 322) = Ethane-1 ol-amine
Chloral-ammonia (fig. 1309, p. 368) = Trichlor-ethane-1 ol-amine
Chloral-imide (fig. 1312, p. 369) = Trichlor-ethane-tri-imine

# Ammonia's Combinations with Acids

Ammonia and acids may combine in two ways, either by addition or by substitution.

## AMMONIUM SALTS

By *addition* ammonium salts are formed, the triad nitrogen assuming the character of a pentad, one of the new valencies receives the acid's hydrogen, the other the rest; for instance, ammonia and hydrochloric acid:

Fig. 1149

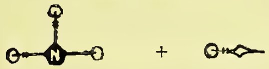
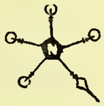


Fig. 1150



Ammonia + hydrochloric acid = Ammonium chloride, sal ammoniac, $NH_4Cl$; volatilises without melting when heated

Fig. 1151

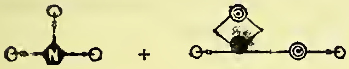
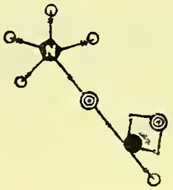


Fig. 1152



Ammonia + formic acid = Ammonium formate, $CH_5NO_2$; m.p. 100°; used in chronic paralysis

Fig. 1153

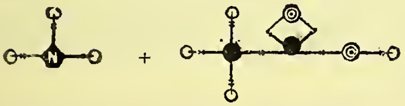
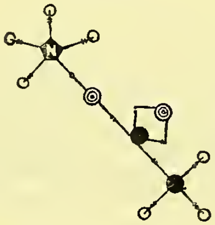


Fig. 1154



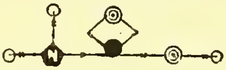
Ammonia + acetic acid = Ammonium acetate, $C_2H_7NO_2$; m.p. 89°; used in influenza complicated with bronchitis, scarlatina, and yellow fever

By *substitution* there is an alternative: the organic acid attaches itself either by its alkyl part or by its carboxyl part. In the former case we call the compounds amido-acids, in the latter case amides (*acid amides* or *amine-acids*).

## AMIDO-ACIDS

From *formic acid* (fig. 666, p. 175):

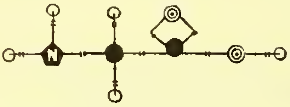
Fig. 1155



Amido-formic acid, carbamic acid, $CH_3NO_2$, may also be looked upon as an amine-acid, and will be mentioned as such afterwards

From *acetic acid* (fig. 667, p. 175):

Fig. 1156

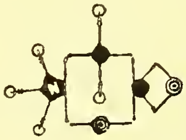


Amido-acetic acid, glycocoll, glycocine, $C_2H_5NO_2$; m.p. 232°; decomposes

Glycocoll (to be carefully distinguished from glycol, fig. 364, p. 76) is found in human urine; in the urine of herbivora it occurs in combination with benzoyl as hippuric acid (fig. 1185, p. 330). When mammalia are fed upon glycocoll it leaves the organism as urea, but from birds it is voided as uric acid.

Amido-acids are rather peculiar compounds: their ammonia-end can combine with acids and their carboxyl-end with bases, at the same time they are in the free isolated state perfectly neutral. It has therefore been suggested (*Ber.* xvi. p. 2650) that the free compounds form a ring, perfectly analogous to betaïne (fig. 1265, p. 355) by joining the carboxyl to the nitrogen, ammonia becoming pentad (ammonium). This structure, *e.g.*, of glycocoll is thus represented:

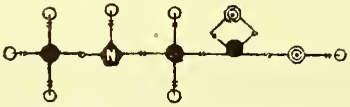
Fig. 1157



In nearly all their derivatives, however, the closed chain is broken and is re-converted into an open chain; they will here be represented in the usual form of the open chain, because thus they are better comparable; besides, as structures with a closed chain, they would have to be referred to the derivatives from quarternary bases (i.e. betaïnes).

If a methyl be introduced into the amido-group of glycocoll we obtain methyl-glycocoll:

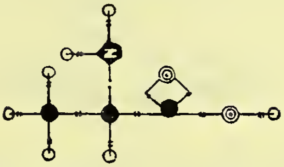
Fig. 1158



Sarcosine, methyl-glycocoll, $C_3H_7NO_2$; m.p. 210°

From *propionic acid* (fig. 669, p. 176):

Fig. 1159

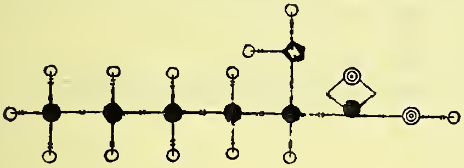


Alanine, α-amido-propionic acid, $C_3H_7NO_2$; melts and sublimes at 255°, partially decomp.; the mercury-salt is used in syphilis. The β-compound is also known

Cystine is formed from alanine by replacing the hydrogen joined to the central carbon-atom by the radical of sulphuretted hydrogen (SH).

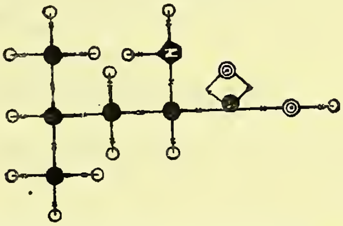
From *caproïc acid* and *iso-butyl-acetic acid* (figs. 673, 674, p. 177):

Fig. 1160



Leucine, α-amido-caproïc acid, $C_6H_{13}NO_2$; m.p. 170°; occurs abundantly in the animal organism as a product of katabolism of proteïds; is the white substance in the 'eyes' of gruyère cheese

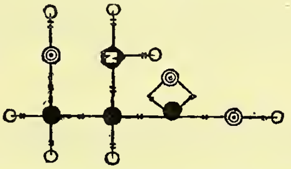
Fig. 1161



Leucine, α-amido-iso-caproïc acid, $C_6H_{13}NO_2$; is derived from vegetable proteïds (*Ber.* xxiv. p. 669)

From *ethylene-lactic acid* (fig. 693, p. 179):

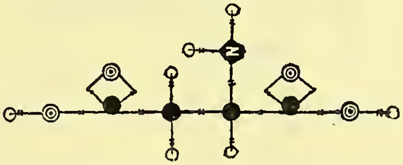
Fig. 1162



Serine, α-amido-ethylene-lactic acid, amido-glyceric acid, $C_3H_7NO_3$

From *succinic acid* (fig. 714, p. 185):

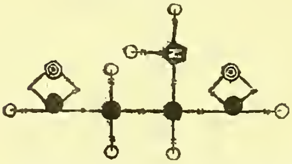
Fig. 1163



Aspartic acid, amido-succinic acid, $C_4H_7NO_4$; may also be looked upon as malic acid, in which hydroxyl is replaced by an amido-group

The *aldehyde* of this acid

Fig. 1164

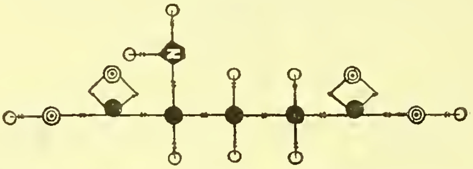


Aspartic aldehyde, $C_4H_7NO_2$; hypothetical

has, however, been suggested as the compound from which proteïds are formed by condensation.

From *glutaric acid* (fig. 719, p. 185):

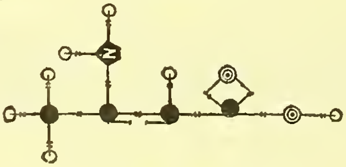
Fig. 1165



Glutamic acid, $C_5H_9NO_4$; m.p. 202°; is nearly always found together with aspartic acid

From *crotonic acid* (fig. 740 p. 190):

Fig. 1166



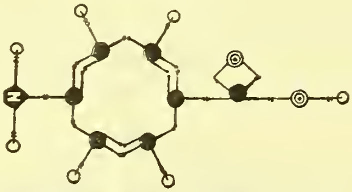
β-Amido-crotonic acid, $C_4H_7NO_2$

Amido-acids formed from the acrylic-acid series with a double bond are collectively distinguished as leuceïnes, whereas those from the fundamental acid series are leucines.

From *cyclo-acids* (p. 208):

Cyclo-acids, being aliphatic acids with a cyclo-hydrocarbon affixed to their alkyl part, can, therefore, form similar compounds; for instance, *benzoic acid* (fig. 812, p. 211).

Fig. 1167



*p*-Amido-benzoic acid, $C_7H_7NO_2$; m.p. 186°

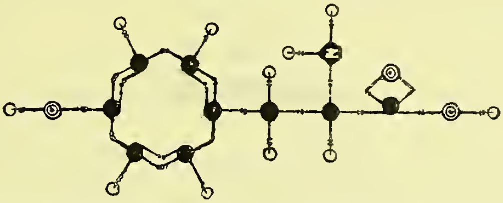
According to the position of the amido-group there are also an ortho-acid (1 : 2), anthranilic acid, and a meta-acid (1 : 3), benzamic acid.

Two or three amido-groups may be fixed to the benzene-ring, forming, theoretically, six di-amido-, and six tri-amido-benzoic acids, five of the former and two of the latter having been prepared.

The amido-group need not always affix itself to the benzene-ring; it can also enter the side-chain.

An instance is *para-coumaric acid* (*vide* p. 216), where ammonia breaks the double bond, gives a hydrogen to one of the valencies, and the rest seizes the other.

FIG. 1168



Tyrosine, β-hydroxy-phenyl-alanine, *p*-hydroxy-phenyl-α-amido-propionic acid, $C_9H_{11}NO_3$; m.p. 235°; occurs in unhealthy liver, molasses, old cheese, pancreatic gland, and is a decomposition product from horn, albumen, feathers, hair, &c.; it may also be looked upon as a combination of *phenol* and *alanine* (fig. 1159, p. 325)

(For further development see p. 363.)

## Future Nomenclature of Amido-acids

Ammonia forming a substituent in the alkyl-part of an acid is distinguished by the prefix *amino-*.

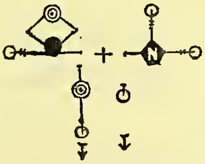
| *Old Nomenclature* | | | *New Nomenclature* |
|---|---|---|---|
| Carbamic acid (figs. 1155 and 1173, pp. 324, 328) | | = | Amino-methanoïc acid, or methanole amide (according to the rule of amides) |
| Glycocoll | (fig. 1156, p. 324) | = | Amino-ethanoïc acid |
| Glycocoll | (fig. 1157, p. 324) | = | Ethanoyl-taïne |
| Sarcosine | (fig. 1158, p. 324) | = | Methyl-amino-ethanoïc acid |
| Alanine | (fig. 1159, p. 325) | = | 2 Amino-propanoïc acid |
| Leucine | (fig. 1160, p. 325) | = | 2 Amino-hexanoïc acid |
| Leucine | (fig. 1161, p. 325) | = | 4 Amino-2 methyl-pentanoïc acid |
| Serine | (fig. 1162, p. 325) | = | 2 Amino-propane-1 ol-oïc acid |
| Aspartic acid | (fig. 1163, p. 325) | = | 2 Amino-butane-dioïc acid |
| Aspartic aldehyde | (fig. 1164, p. 326) | = | Amino-butane-dial |
| β-Amido-crotonic acid | (fig. 1166, p. 326) | = | 2 Amino-2 butenoïc acid |

## AMIDES AND ACID AMIDES (or AMINIC ACIDS)

These are formed, as already mentioned, by affixing to ammonia an acid by its carboxyl-end; a molecule of water is separated, the hydroxyl of which is taken from the carboxyl, ammonia contributing the hydrogen needed to form water. Thus ammonia forms—

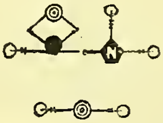
From *formic acid* (fig. 666, p. 175):

FIG. 1169



=

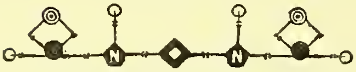
FIG. 1170



Formic acid + ammonia = Water + formamide, $CH_3NO$; b.p. 192°

The *mercury*-compound :

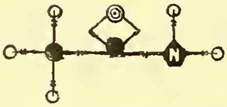
Fig. 1171



Mercury-formamide, $Hg(CH_2NO)_2$ ; used for subcutaneous injections

From *acetic acid* (fig. 667, p. 175) :

Fig. 1172

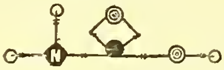


Acetamide, $C_2H_5NO$ ; m.p. 82°

The two remaining hydrogens of ammonia may also be substituted by acid radicals in the same way as the first hydrogen, producing secondary or tertiary amides ; or they may be replaced by alcohol radicals (alkyls forming alkylated amides).

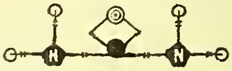
Dibasic acids (p. 184), having two carboxyls, may have an ammonia rest affixed to either one or both of them ; in the former case the compounds are acid amides or amine-acids, in the latter amides. *Carbonic acid*, therefore, forms two combinations with ammonia, one of which has already been mentioned, viz. carbamic acid (fig. 1155, p. 324), which, besides being considered a derivative of formic acid, may just as well be looked upon as formed from carbonic acid.

Fig. 1173



Carbamic acid, $CH_3NO_2$ ; cannot exist in free state, splitting up into carbon dioxide and ammonia ; but as soon as a base, an alcohol, or even another amido-group lends a helping hand by pushing the hydroxyl away, its existence as a salt, ether, amide, &c., is secured

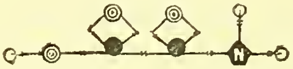
Fig. 1174



Carbamide, urea, $CH_4N_2O$ ; m.p. 132° ; it is the final decomposition product from the oxidation of nitrogenous compounds (albumen &c.), just as carbonic acid is from the oxidation of hydrocarbons and their oxygen-derivatives. An adult produces about 30 grammes urea daily ; the urine contains 20–30 grammes in a litre

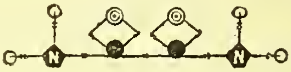
*Oxalic acid* (fig. 712, p. 184) forms similarly, two compounds :

Fig. 1175



Oxamic acid, $C_2H_3NO_3$ ; m.p. 173° ; decomp.

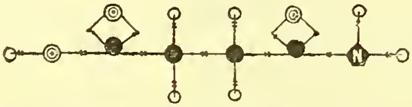
Fig. 1176



Oxamide, $C_2H_4N_2O_2$ ; splits up on heating

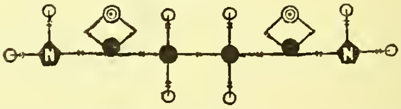
and *succinic acid* (fig. 714, p. 185) :

Fig. 1177



Succinamic acid, $C_4H_7NO_3$ ; m.p. 300° ; being at the same time converted into succinimide

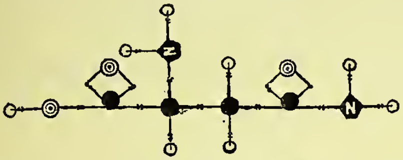
Fig. 1178



Succinamide, $C_4H_8N_2O_2$ ; being converted into succinimide at 200°

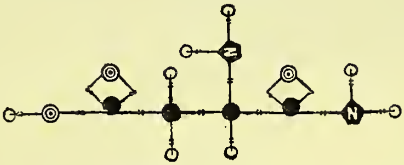
If, instead of succinic acid, we employ *amido-succinic acid* (fig. 1163, p. 325) we may have two structures according to which hydroxyl is replaced:

Fig. 1179 A



β-Asparagine, amido-succinamic acid, aspartic amide, $C_4H_8N_2O_3$

Fig. 1179 B



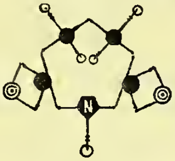
α-Asparagine $C_4H_8N_2O_3$

The first of the figures represents ordinary dextro-rotatory asparagine, the second is optically inactive and a laboratory product.

Ordinary asparagine is widely distributed in the vegetable world, particularly in plants, or parts of plants, growing in the dark, *e.g.* asparagus. The peculiar smell of urine after eating asparagus is not due to asparagine, as formerly believed, but is now attributed to ethyl-mercaptan (fig. 992, p. 281).

When succinamide is heated to 200° one of the amido-groups leaves, taking a hydrogen-atom along with it from the amido-group at the other end, thus leaving a free valency at each end. The consequence is that the chain bends and forms a closed chain:

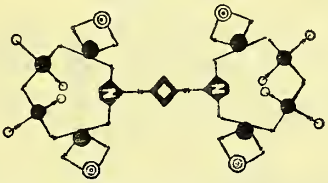
Fig. 1180



Succinimide, $C_4H_5NO_2$; m.p. 125°; the same happens to succinamic acid at 300°, water being dropped

The hydrogen attached to the nitrogen-atom may be replaced by some metals. Mercury, which is a dyad element, will replace the hydrogen-atoms of two molecules of succinimide.

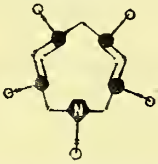
Fig. 1181



Mercury succinimide, $Hg(C_4H_4NO_2)_2$; used for subcutaneous injections; it has no effect upon albuminous fluids, and is therefore well adapted for this application

The two oxygen-atoms of succinimide may be removed, leaving four free valencies. In order to accommodate these the hydrogens inside the ring will leave their places, and remove to the valencies outside the ring, so that double bonds may be formed, and a compound of this structure will result.

Fig. 1182

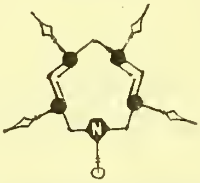


Pyrrol, $C_4H_5N$; b.p. 131°; occurs in coal-tar and bone-oil

Pyrrol is analogous to furfurane (fig. 941, p. 260) and thiophene (fig. 1015, p. 285), all three being di-ethylenes, which are formed into closed chains through the assistance of oxygen, sulphur, or nitrogen. Compare also succinimide, above, and succinic anhydride (fig. 716, p. 185).

When the four hydrogen-atoms bound to carbon-atoms in pyrrol are replaced by iodine it is converted into

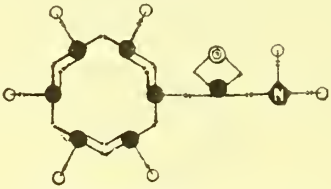
Fig. 1183



Iodol, tetra-iodo-pyrrol, $C_4HI_4N$ ; decomp. on heating; non-poisonous; used instead of iodoform as an antiseptic; it is also a local anæsthetic

From *benzoic acid* is derived

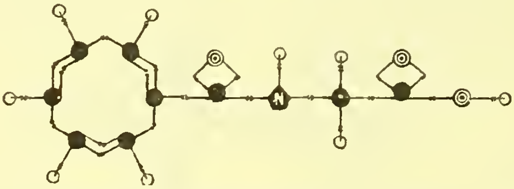
Fig. 1184



Benzamide, $C_7H_7NO$ ; m.p. 130°

By joining *acetic acid* by its alkyl-part to the amido-group we have the structure of hippuric acid:

Fig. 1185



Hippuric acid, benzamido-acetic acid, $C_9H_9NO_3$ ; decomp. on heating

It is found in the urine of herbivora; also in that of carnivora after taking benzoic acid internally. It may be looked upon as a joining of *benzoyl* and *glycocoll* (fig. 1156, p. 324), the latter being found in the bile as glycocholic acid, which explains the production of hippuric acid in the human urine after eating benzoic acid.

Eugenol-acetic-amide, $C_{12}H_{15}NO_3$, m.p. 110°, formed from *eugenol-acetic acid* (fig. 921, p. 253) by substituting an amido-group for carboxyl's hydroxyl, is recommended as a local anæsthetic.

(For *anilides*, which strictly belong to this class, *vide* p. 341; and for further development, p. 368.)

### Future Nomenclature of Amides and Acid Amides

The nomenclature of these compounds is to be formed from the corresponding hydrocarbons (not from the acids) and the suffix *-amide*, or *-imide*, in the case of the group NH closing a chain. An exception is urea, which retains its name. Amidoximes (a class we have not had occasion to mention) also retain their names with aforesaid restriction.

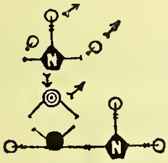
*Old Nomenclature* — *New Nomenclature*

Formamide (fig. 1170, p. 327) = Methanamide
Acetamide (fig. 1172, p. 328) = Ethanamide
Oxamic acid (fig. 1175, p. 328) = Ethanamide acid (?)
(Ethanoyloïc (acid) amide ?)
Oxamide (fig. 1176, p. 328) = Ethanediamide
Succinamic acid (fig. 1177, p. 328) = Butanamide acid (?)
Succinamide (fig. 1178, p. 328) = Butanediamide
Succinimide (fig. 1180, p. 329) = Butanimide
Asparagine (fig. 1179, p. 329) = 2 Amino-butanamide acid (?)

## Amidines

The carbonyl-oxygen in amides may be replaced by an imido-group, and such compounds are distinguished as **amidines**. The free amidines are unstable, but they form with acids stable salts.

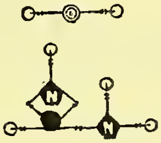
Fig. 1186



Formamide + ammonia

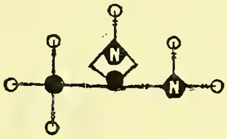
=

Fig. 1187



Formamidine, methenylamidine, $CH_4N_2$ ; m.p. 81°

Fig. 1188



similarly : Acetamidine, ethenylamidine, $C_2H_6N_2$ ; decomp. on heating

Mention is due to these compounds as a class, otherwise they are of little interest to us.

### Future Nomenclature of Amidines

The suffix *-amidine* is retained as the distinguishing class-designation, but, like amides, amidines are considered derivatives from hydrocarbons, and not from acids.

*Old Nomenclature* — *New Nomenclature*

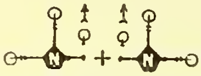
Formamidine (fig. 1187, above) = Methanamidine
Acetamidine (fig. 1188, above) = Ethanamidine

In the case of substitutions in one or both nitrogen-groups it has been suggested to split up the suffix *-amidine* into *amid-imidine*, e.g. *ethanamid-ethylimidine*.

## Hydrazine

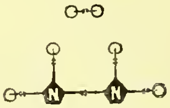
Ammonia is also able to combine with itself by removing one pair of hydrogen-atoms; the ensuing compound is termed hydrazine.

Fig. 1189



Two molecules of ammonia =

Fig. 1190



Hydrazine, $N_2H_4$ (*Ber.* xx. p. 1632)

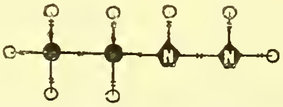
Hydrazine, which has been known only the last few years, is a colourless gas fuming in the air, and is a strong base. Its hydrogen-atoms may be substituted by hydrocarbons and derivatives. If the substitution takes place in the same nitrogen-atom, the derivatives are styled hydrazine-compounds; but hydrazo-compounds if hydrogen in each of the two amido-groups is replaced.

### HYDRAZINE-COMPOUNDS

(Asymmetrical or *a*-hydrazines)

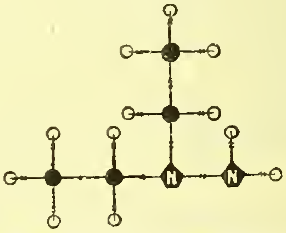
According as one or two hydrogen-atoms in the same amido-group are replaced, they are distinguished as primary or secondary hydrazines, *e.g.*

Fig. 1191



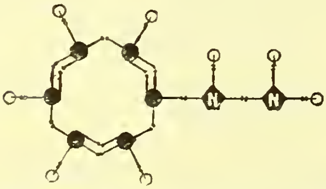
Ethyl-hydrazine, $C_2H_8N_2$; b.p. 100°; primary

Fig. 1192



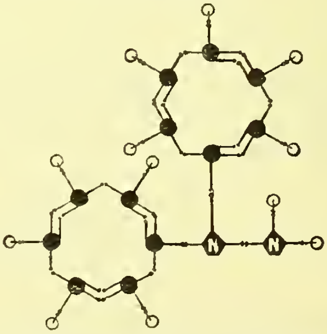
Di-ethyl-hydrazine, $C_4H_{12}N_2$; b.p. 96–99°; secondary

Fig. 1193



Phenyl-hydrazine, $C_6H_8N_2$; m.p. 23°; primary

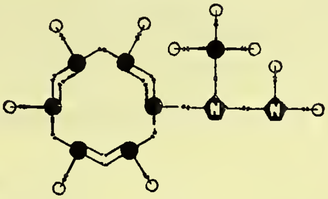
Fig. 1194



Di-phenyl-hydrazine, $C_{12}H_{12}N_2$; oily fluid; secondary

Also *mixed secondary hydrazines* exist:

Fig. 1195



α-Methyl-phenyl-hydrazine, $C_7H_{10}N_2$; b.p. 227°, under 745 mm. pressure, slightly decomposing

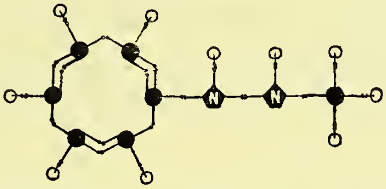
## HYDRAZO-COMPOUNDS

### (Symmetrical or β-hydrazines)

Hydrazo-compounds of the aliphatic series alone are not known; cyclo-compounds and their derivatives are, however, prepared in great numbers, as well as mixed cyclo- and aliphatic compounds.

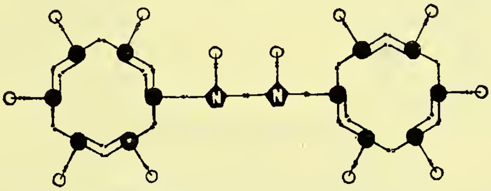
As the simplest examples, may be mentioned

Fig. 1196



Hydrazo-methyl-phenyl, *s*- or β-methyl-phenyl-hydrazine, $C_7H_{10}N_2$; b.p. 180°; a volatile unstable oil, used in the preparation of *antipyrine*

Fig. 1197



Hydrazo-benzene, $C_{12}H_{12}N_2$; m.p. 131°

(For further development of hydrazines and hydrazo-compounds, *vide* p. 380.)

## Future Nomenclature of Hydrazine-compounds

The conventional distinction between symmetrical and asymmetrical hydrazines is maintained, the former by interposition of the word *hydrazo* between the substituting *hydrocarbons* in each amido-group, the latter by the suffix *-hydrazine* added to the names of the substituting *hydrocarbon-radicals.*

We will in the undermentioned examples suppose that benzene and phenyl are to retain their old names.

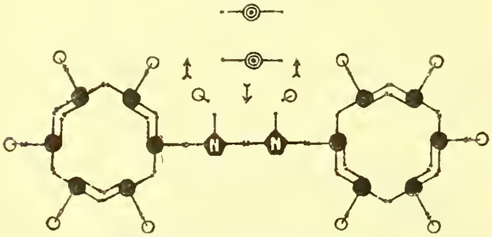
| *Old Nomenclature* | | | *New Nomenclature* |
|---|---|---|---|
| Ethyl-hydrazine | (fig. 1191, p. 332) | = | No change |
| Di-ethyl-hydrazine | (fig. 1192, p. 332) | = | No change |
| Phenyl-hydrazine | (fig. 1193, p. 332) | = | No change |
| Di-phenyl-hydrazine | (fig. 1194, p. 332) | = | No change |
| Methyl-phenyl-hydrazine | (fig. 1195, p. 333) | = | Phenyl-methyl-hydrazine |
| Hydrazo-methyl-phenyl | (fig. 1196, p. 333) | = | Benzene-hydrazo-methane |
| Hydrazo-benzene | (fig. 1197, p. 333) | = | Benzene-hydrazo-benzene |
| Acetyl-phenyl-hydrazine | (fig. 1356, p. 380) | = | Benzene-hydrazo-ethanoyl (?) |
| Ethoxy-hydracetine | (fig. 1357, p. 381) | = | Ethane-oxy-benzene-hydrazo-ethanoyl (?) |

Whether *ethanoyl*, which is a radical, is correct in the last two examples, I am unable to say; in full accord with the hydrocarbon-name on the other side of the hydrazo-group it ought, perhaps, to be ethanal, which is not a radical.

## Azo-oxy-compounds

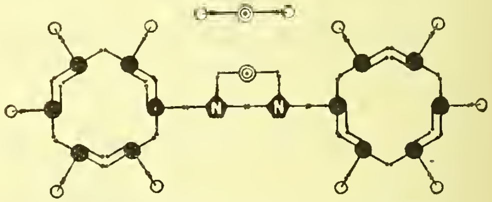
When we let a molecule of oxygen react upon hydrazo-compounds one atom seizes the two hydrogen-atoms in the imido-groups forming water, and the other oxygen takes their place.

Fig. 1198



=

Fig. 1199

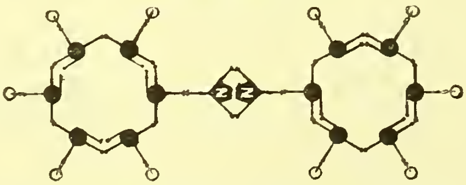


Hydrazo-benzene + oxygen = Azo-oxy-benzene, $C_{12}H_{10}N_2O$; m.p. 36°

## Azo-compounds

By suitable reducing agents the oxygen can again be removed without any substitution taking place; the two free imido-valencies will then join, forming a double bond between the two nitrogen-atoms; the resulting compound is termed an azo-compound.

Fig. 1200

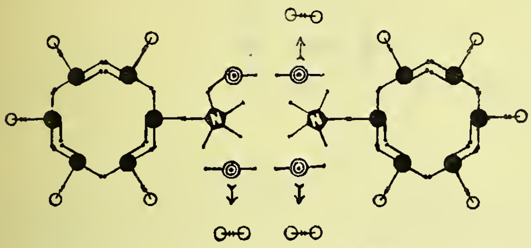


Azo-benzene, $C_{12}H_{10}N_2$; red crystals; m.p. 68°

Hydrazo- and azo-compounds are, for the manufacture of dyes, of great significance. From them are prepared colours varying from yellow, through orange and golden yellow, to brown. Aniline-yellows, chrysoïdines, phenylenediamine-brown, indulines (blue), and tropæolines are amongst them. The last one is also a valuable alkaline indicator in titration.

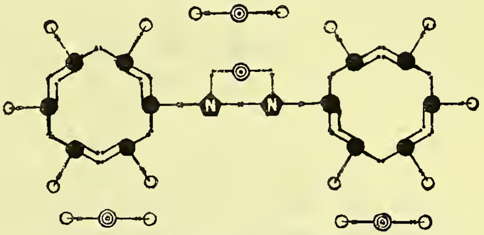
All these azo-oxy-, azo-, and hydrazo-compounds are sometimes collectively distinguished as azo-compounds; practically they are derived from nitro-benzene (fig. 1090, p. 306) by the successive action of reducing and oxidising agents in this way:

Fig. 1201



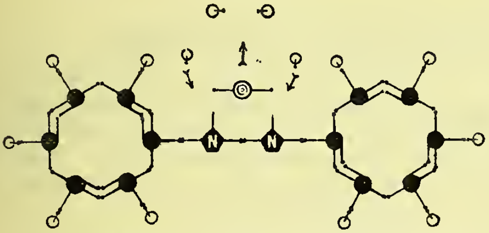
Two molecules of nitro-benzene – three atoms of oxygen =

Fig. 1202



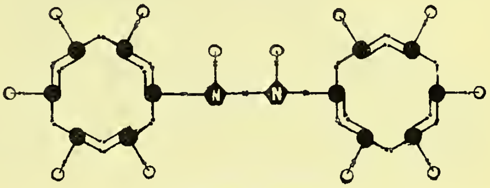
Azo-oxy-benzene + three molecules of water

Fig. 1203



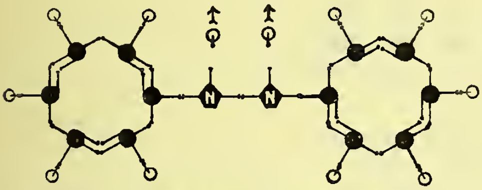
Azo-oxy-benzene – oxygen + two hydrogen atoms =

Fig. 1204



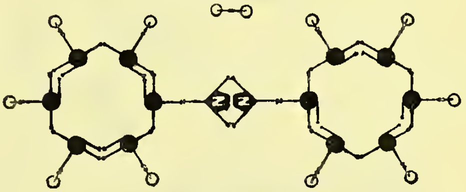
Hydrazo-benzene

Fig. 1205



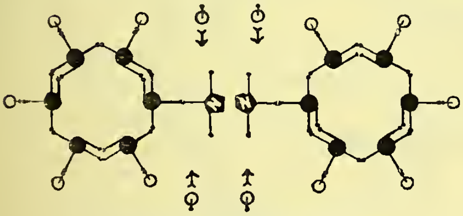
Hydrazo-benzene – two hydrogen-atoms =

Fig. 1206



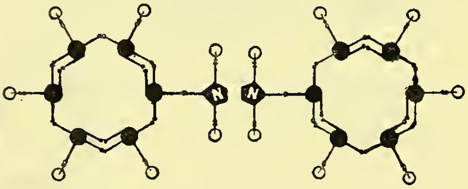
Azo-benzene

Fig. 1207



Azo-benzene + four hydrogen-atoms =

Fig. 1208



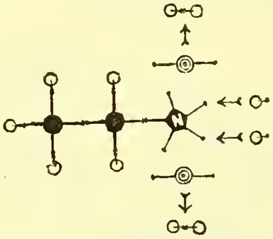
Two molecules of amido-benzene (aniline, fig. 1111, p. 313)

From nitro-benzene, through azo-oxy-benzene, hydrazo-benzene, and azo-benzene, we finally arrive at *amido-benzene.*

Azo-oxy- and azo-compounds are coloured bodies, hydrazo-compounds mostly colourless.

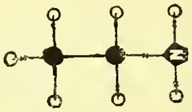
If we try the same process upon *aliphatic nitro-compounds* we shall find they are reduced to amido-compounds without passing through the intermediary stages of the nitro-cyclo-compounds

FIG. 1209



=

FIG. 1210



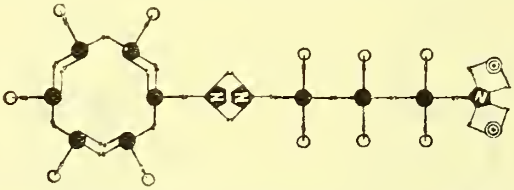
Nitro-ethane + three molecules of hydrogen = Ethylamine (fig. 1109, p. 313)

For this reason the azo-compounds of the aliphatic series are not known, it is, however, probable that there are intermediary stages in these transformations, not by the co-operation of *two* molecules, as in the cyclo-compounds, but by momentary, still successive, conversion of *single* nitro-molecules through nitroso- and hydroxylamine-stages into amido-compounds.

## Mixed Azo-compounds and Diazo-compounds

Although no azo-compounds have been prepared exclusively from aliphatic compounds, chemists have succeeded in producing a sort of compromise-compound in which aliphatic nitro-derivatives occupy one side of the azo-group, the other being retained by the benzene-derivative. They are termed mixed compounds, which designation also includes such azo-compounds in which the benzene-derivatives on each side of the azo-group are not identical.

FIG. 1211



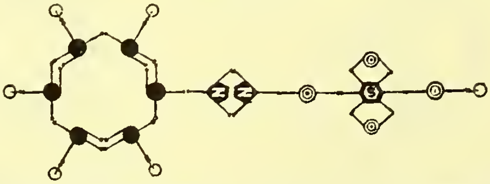
Azo-nitro-propyl-phenyl, $C_9H_{11}N_3O_2$; m.p. 98°

Such azo-nitro-compounds are brilliant dyes.

Finally we can on one side of the azo-group place an electro-negative element, such as chlorine, iodine, bromine, an acid- or a basic-group: these compounds are termed diazo-compounds (the logic of which designation is not obvious).

Combination with *sulphuric acid*:

FIG. 1212



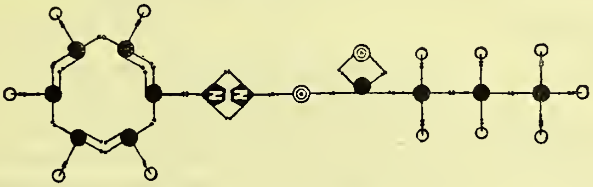
Acid diazo-benzene-sulphate, $C_6H_6N_2SO_4$; explodes at 100°

This is an acid salt because sulphuric acid is di-basic. With mono-basic acids neutral salts are formed.

The free diazo-benzene, where the sulphuric group in the above structure is replaced by hydroxyl, is a thick yellow oil. It is readily decomposed, evolving nitrogen. The same decomposition takes place with diazo-compounds in the (alkaline) blood. Animals, therefore, quickly die, exhibiting symptoms of suffocation after taking such compounds.

Combination with *butyric acid* :

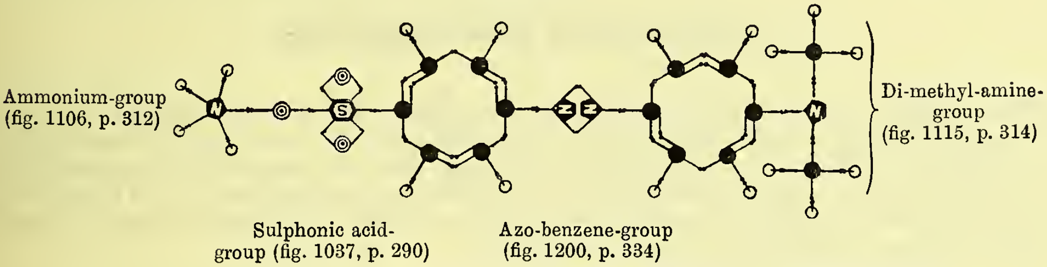
FIG. 1213



Tyrotoxicon, diazo-benzene-butyrate, $C_{10}H_{12}N_2O_2$ ; the poisonous alkaloid (ptomaïne) of milk and cheese (*Lauder Brunton*, p. 60)

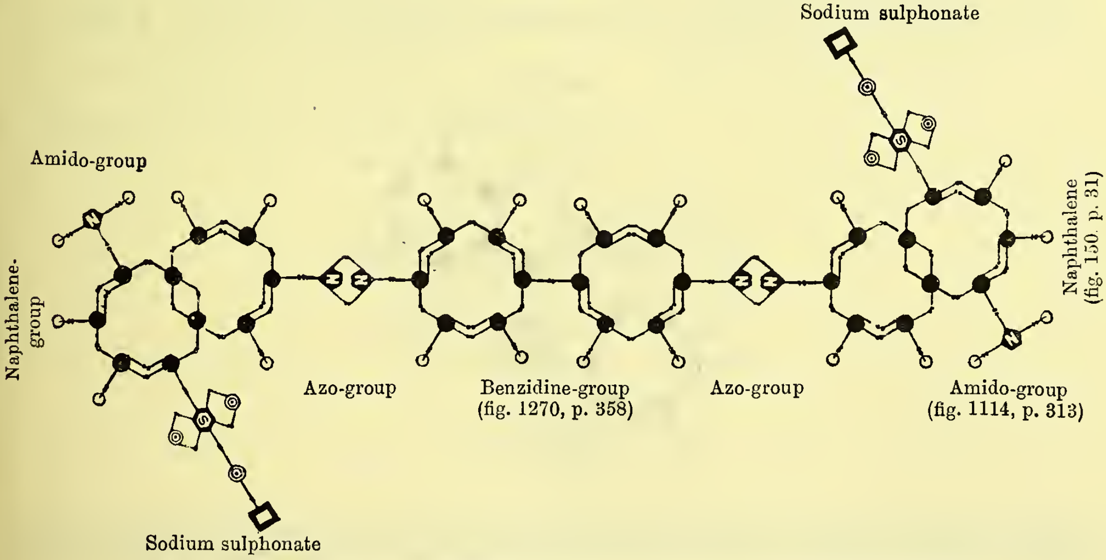
The structure of one or two dyes may interest.

FIG. 1214



Methyl-orange, $C_{14}H_{18}SN_4O_3$ ; is also used as a delicate indicator in alkalimetrical titrations

FIG. 1215



Congo-red, *benzidine-tetrazo-di-sodium-naphthionate* (*vide* p. 351). Compounds with two azo-groups are termed tetrazo compounds

## Future Nomenclature of Azo-compounds

The class distinctions hitherto in use are retained, the committee having allowed the opportunity to pass of getting rid of the misnomer *diazo.*

The compounds attached to the group of nitrogens are to be separated in the nomenclature by the words *azoxy*, *azo*, or *diazo* in the same way as they are in the structure.

| *Old Nomenclature* | | *New Nomenclature* |
|---|---|---|
| Azo-oxy-benzene | (fig. 1199, p. 334) = | Benzene-azoxy-benzene |
| Azo-benzene | (fig. 1200, p. 334) = | Benzene-azo-benzene |
| Azo-nitro-propyl-phenyl | (fig. 1211, p. 336) = | Benzene-diazo-3 nitro propane |
| Acid-diazo-benzene-sulphate | (fig. 1212, p. 336) = | Benzene-diazo-(acid ?) sulphate |
| Tyrotoxicon | (fig. 1213, p. 337) = | Benzene-diazo-butyrate |

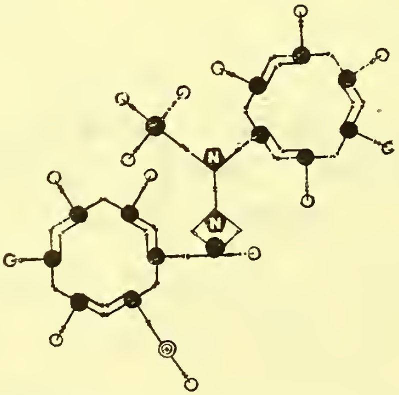
# Hydrazones and Osazones

Phenyl-hydrazine (fig. 1193, p. 332) joins aldehydes, ketones, aldehyde-acids, ketone-acids (p. 227), and generally compounds with one or more carbonyls in the same way as we saw hydroxylamine (fig. 1133, p. 319) do it. If one phenyl-hydrazine joins, the compounds are termed hydrazones. In the case of alcohol-aldehydes and alcohol-ketones (carbohydrates, p. 151), di-aldehydes (p. 132), di-ketones (p. 140), or, generally, compounds with two carbonyls, two phenyl-hydrazines may join, and these compounds are termed osazones.

Examples of these compounds are—

From *salicylic-aldehyde* (fig. 559, p. 135) and *methyl-phenyl-hydrazine* (fig. 1195, p. 333):

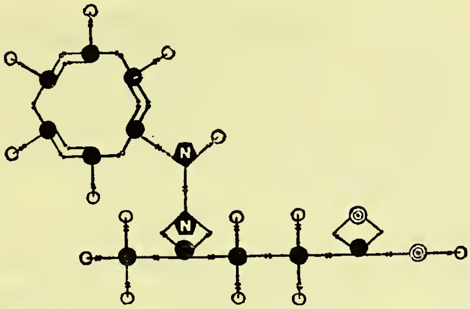
Fig. 1216



Agathine, salicyl-α-methyl-phenyl-hydrazone, $C_{14}H_{14}N_2O$; m.p. 74° (*Ph. C.* xxxiii. p. 383; *D. Med. Ztg.* 1892, p. 489); useful in rheumatic affections; analgesic. Although methyl-phenyl-hydrazine is poisonous, this derivative does not appear to be so

From *levulinic acid* (fig. 855, p. 228) and *phenyl-hydrazine*:

FIG. 1216 A

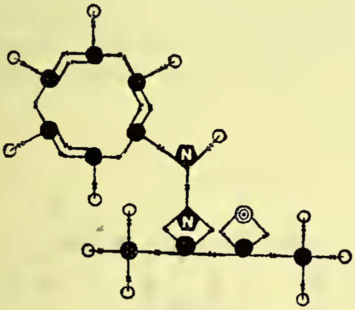


Antithermine, phenyl-hydrazine-levulinic acid, $C_{11}H_{14}N_2O_2$; m.p. 108°; antifebrilium, but unreliable

It is generally, but incorrectly, referred to as a phenyl-hydrazine.

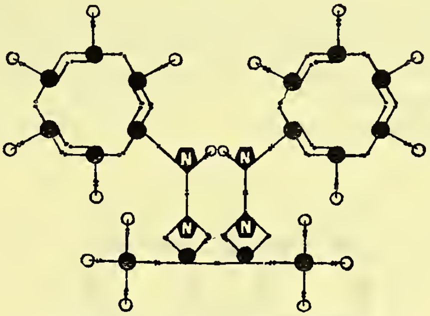
From *diacetyl* (fig. 576, p. 140) and *phenyl-hydrazine*:

FIG. 1217



Diacetyl-hydrazone, $C_{10}H_{12}N_2O$; m.p. 133°

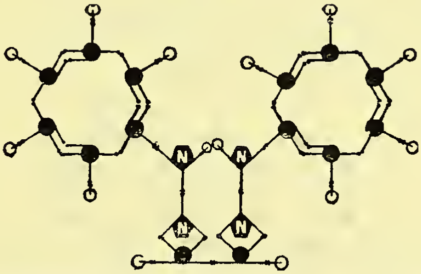
FIG. 1218



Diacetyl-osazone, $C_{16}H_{18}N_4$; m.p. 239°

From *glyoxal* (fig. 545, p. 132) and *phenyl-hydrazine*:

FIG. 1219



Glyoxalosazone, $C_{14}H_{14}N_4$; red crystals; m.p. 155°

Hydrazones and osazones from sugars form well crystallisable compounds, and have therefore lately been very useful in the synthetical preparation of them. The process has been described on pp. 154 and 155.

### Future Nomenclature of Hydrazones and Osazones

The names of hydrazones should, according to the Congress resolutions, be formed by converting the terminations *-al* and *-one* of aldehydes and ketones into the suffix *-hydrazone*, or into *dihydrazone* in the case of osazones, instead of the now usual form of *phenyl-hydrazones* and *phenyl-osazones.* The editor of *Berichte* objects to the omission of the word *phenyl*, because other hydrazines enter into aldehydes and ketones exactly in the same way as phenyl-hydrazine proper. This objection seems unimpeachable, and the suffix -phenyl-hydrazone will probably have to be adopted, wherefore I substitute it in the following examples :

*Old Nomenclature* — *New Nomenclature*

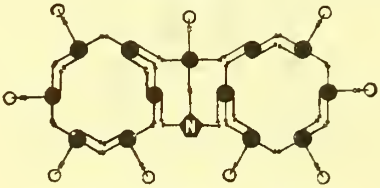
Diacetyl-hydrazone (fig. 1217) = Butane-3 one-2 phenyl-hydrazone
Diacetyl-osazone (fig. 1218) = Butane-2 : 3 diphenyl-hydrazone
Glyoxal-osazone (fig. 1219) = Ethane-diphenyl-hydrazone

## Acridines and Azines (Phenazines)

There are two groups which are theoretically interesting because they may be considered anthracenes (fig. 307, p. 59), in which either one or both groups CH in the middle- (ethylene-) group are substituted by nitrogen ; otherwise they are of no special value here, being chiefly employed to produce dyes, many brilliant enough, as *mauveïne*, *magdala-red*, *chrysaniline*, *safranines*, &c.

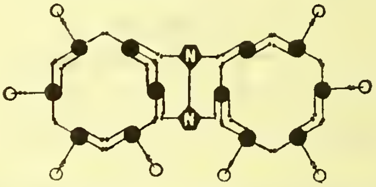
Their structures are

Fig. 1220



Acridine, $C_{13}H_9N$ ; m.p. 107°

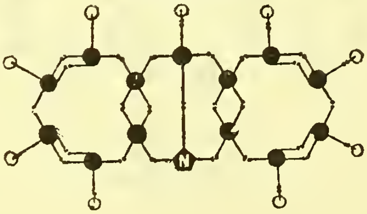
Fig. 1221



Phenazine, $C_{12}H_8N_2$ ; yellow crystals ; m.p. 171°

These compounds are generally represented as consisting of three interlocked hexagons :

Fig. 1222



It is evidently less correct, and has already caused some confusion in the nomenclature by giving the same name, *azines*, to a different series of compounds (vide *azines*, *diazines*, &c., pp. 388, 389).

# Further Development of Ammonia-combinations

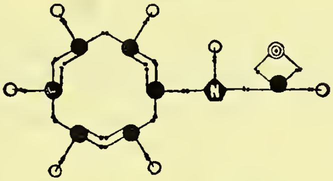
## DERIVATIVES FROM PRIMARY AMMONIA-BASES (*vide* p. 313)

Beyond those already mentioned, no other primary ammonia-base derived from aliphatic hydrocarbons calls for our attention. There are, however, derivatives from aromatic amines which are of special importance, including some very modern remedies. The first to be mentioned are those derived from aniline by replacing a hydrogen-atom of the amido-group by the radical of an acid. They are rather numerous, and belong strictly to amides, but are as a class distinguished as

### Anilides

If we combine *formic acid* and *aniline* by separating a molecule of water (hydroxyl from the acid + a hydrogen-atom from the amido-group) we obtain

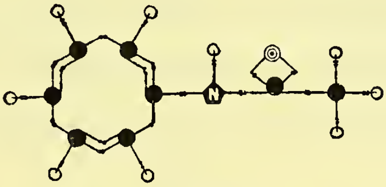
Fig. 1223



Formanilide, $C_7H_7NO$; m.p. 46°; acts, subcutaneously injected, as an anæsthetic, and externally as a styptic

By substituting *acetic acid* for formic acid we have

Fig. 1224



Acetanilide, antifebrine, phenyl-acetamide, $C_8H_9NO$; m.p. 114°; hypnotic and antipyretic

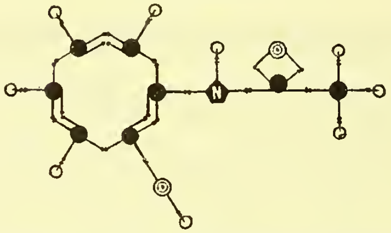
Exodyne is a so-called patent medicine, containing acetanilide, sodium salicylate, and sodium bi-carbonate.

Phenolide is a mixture of acetanilide and sodium bicarbonate.

Antikol is acetanilide, sodium bicarbonate, and tartaric acid (*Ph. Rundschau*, 1892, No. 8, p. 186).

When *acetic acid* is combined with o-*amido-phenol* (*vide* p. 321) instead of with aniline, we produce

FIG. 1225

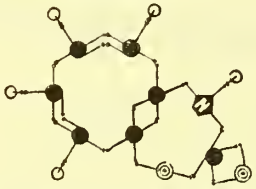


Hydroxy-acetanilide, aceto-amido-phenol, $C_8H_9NO_2$; m.p. 201°

which is meant to be an improvement upon acetanilide.

By heating, methyl goes away as methane, complementing its hydrogens from the hydroxyl; the two free valencies thus created, one in the acetyl-group, the other in the hydroxyl-group, unite, forming with benzene an interlocked ring (pentagon).

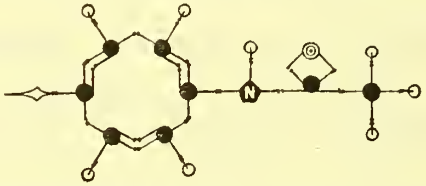
FIG. 1226



Carbonyl-amido-phenol, oxycarbanil, anhydro-amido-phenyl-carbonic acid, $C_7H_5NO_2$; m.p. 137°; antipyretic; it is the form in which acetanilide leaves the organism of carnivora

By substituting *bromine* or *iodine* for the hydrogen in para-position in acetanilide, we obtain

FIG. 1227



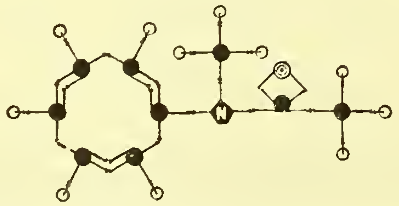
Iodo-acetanilide, iodo-antifebrine, $C_8H_8ClNO$; m.p. 181°·5; is not a febrifuge

Bromo-acetanilide, *bromo-antifebrine, antisepsine,* $C_8H_8BrNO$, antipyretic, sedative, and antiseptic.

Salbromalide, *salicyl-bromanilide* or *antinervine* is a mixture of ammonium-bromide, salicylic acid, and acetanilide.

If the last hydrogen in the amido-group in acetanilide is substituted by methyl, the product is called

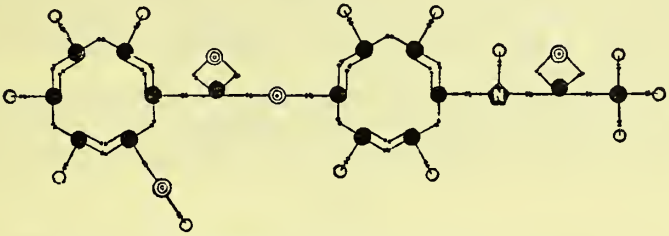
FIG. 1228



Exalgine, methyl-acetanilide, methanilide, $C_9H_{11}NO$; m.p. 101°; analgesic and antiseptic

Further, if we substitute the para-hydrogen of acetanilide by *salicylic acid*, acetanilide salicylic ether is formed, the trade name for which is

FIG. 1229

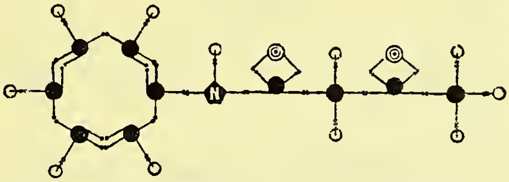


Salophene, $C_{15}H_{13}NO_4$; m.p. 187°

It is intended to be used in lieu of salol (fig. 903, p. 245); it may be considered a combination of salol and acetamide (fig. 1172, p. 328): acetyl-*p*-amido-salol. The object of introducing the latter into the former is to lessen the sometimes toxic effects of salol. *Salophene* should not be confounded with *saliphene* (fig. 1247, p. 349).

With *aceto-acetic acid* (fig. 853, p. 227) aniline forms an anilide:

FIG. 1230



Aceto-acetanilide, $C_{10}H_{11}NO_2$; m.p. 85°

*Methylamine* (fig. 1108, p. 313) will join *aceto-acetanilide*, and form from the side-chain a cyclo-compound, separating water and hydrogen, a molecule of each (*Ber.* xxv. p. 1869):

FIG. 1231

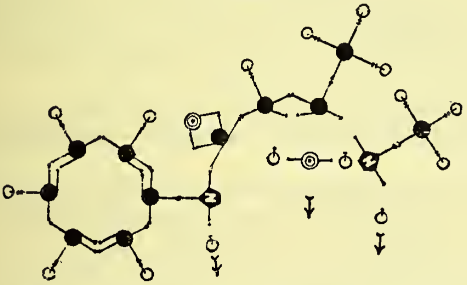
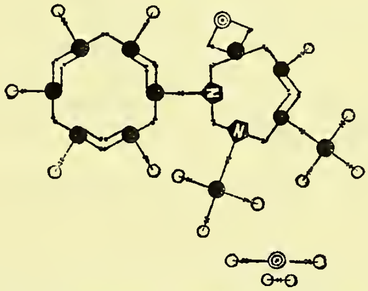


FIG. 1232



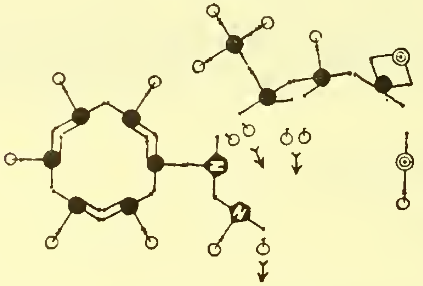
Aceto-acetanilide + methylamine — water and hydrogen = Antipyrine, phenazone, di-methyl-oxy-quinizine, anodynine, metozine, parodyne, analgesine, sedatine, phenyl-di-methyl-pyrazolone, $C_{11}H_{12}N_2O$; m.p. 113°; hypnotic and antipyretic

This is known as Knorr's antipyrine. Practically it has to be prepared in a more complex way by heating a mixture of aceto-acetic ethyl-ether (fig. 868, p. 232) and phenyl-hydrazine (fig. 1193, p. 332), whereby phenyl-methyl-pyrazolone is obtained (i.e. antipyrine + H and $-CH_3$), to which the necessary methyl is added by heating with methyl-iodide.

Before proceeding with antipyrine we shall mention an isomer. Knorr's antipyrine is protected by a patent, and, on account of the enormous consumption it enjoys, tremendous efforts have been, and are still, being made to find some other way of preparation. Organic chemistry is the only one that has as yet profited by these exertions; no result has been obtained that could be turned to any practical account by inventors.

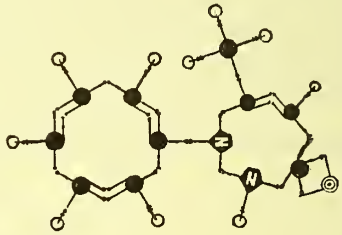
The most interesting of these attempts to form antipyrine is the experiment with butyric acid (fig. 670, p. 176) and phenyl-hydrazine. The brom-ethyl-ether of butyric acid was used, but in order not to unnecessarily complicate matters we will for the purpose of illustration again use the simple acid.

Fig. 1233



Phenyl-hydrazine + butyric acid

Fig. 1234



Phenyl-methyl-iso-pyrazolone, $C_{10}H_{10}N_2O$; m.p. 167°

The cause of isomerism is that butyric acid unfortunately turns the wrong ends to phenyl hydrazine, as will be seen by comparing this compound with the preceding one. The missing methyl-group may be introduced as before through methyl-iodine. This is known as Böhringer's (or *iso-*) antipyrine, but it has not found any therapeutical employment (compare also p. 382).

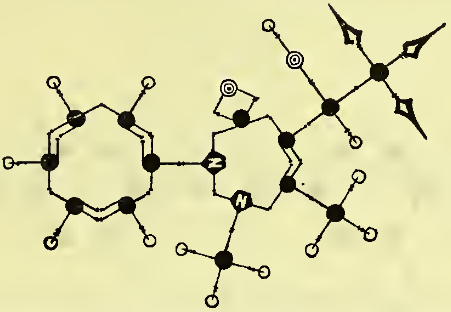
Attempts at improving upon antipyrine have not been wanting. *Iodine* and *bromine* have, of course, been introduced: several combinations seem to be possible; by addition, breaking the double bond in the pyrazolone ring, or by substitution of the H either in pyrazolone's CH group or in the benzene-ring. Except one with the iodine-substitution in the benzene-ring (*iodo-pyrine*), they do not seem to be of any use as medicines, as they go right through the system without any change.

Further, through substitution by *ethylene hydroxide* (the radical of glycol, fig. 364, p. 76) of the methyl affixed to nitrogen, the compound receiving the name of oxethyl-methyl-phenyl-pyrazolone.

Quite recently, after having tried the introduction of *ethoxyl* (fig. 389, p. 81) into the phenyl-group in para-position, but without producing any therapeutically useful compound, *methyl* was tried, also in para-position, and the resulting compound is favourably spoken of as a modified antipyrine. The methyl transforms the phenyl into tolyl (fig. 177, p. 34); therefore this new compound has been termed tolypyrine, the systematical name being p-*tolyl-di-methyl-pyrazolone*. Just as antipyrine combines with salicylic acid (*vide* fig. 1236) to form salipyrine, so this new compound unites with the same acid, producing salicylic *p*-tolyl-di-methyl-pyrazolone, which has the trade name tolysal, $C_{19}H_{20}N_2O_4$, m.p. 101–102° (*Ph. C.* xxxiii. p. 715).

Several combinations of antipyrine and chloralhydrate (fig. 977, p. 272) have been made. One of them enjoying the title of dehydro-tri-chloraldehyde-phenyl-di-methyl-pyrazolone has probably this structure:

FIG. 1235



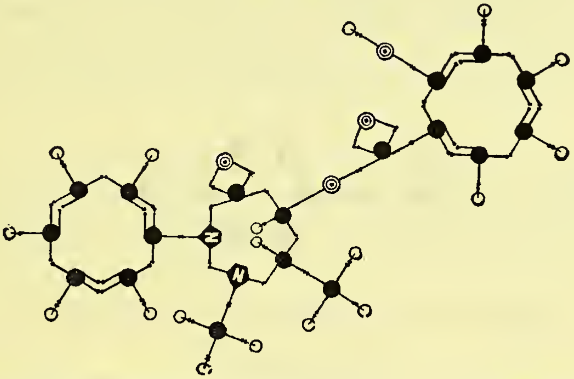
$C_{13}H_{13}Cl_3N_2O_2$ ; it is insoluble in water, and melts at 186°

Another which has to content itself with the shorter name of **hypnal** is also composed of one molecule of chloral and one molecule of antipyrine ; melts, however, at 67° ; nothing is known of its structure.

**Butyl-hypnal** is a similar combination of *butyl-chloral-hydrate* (fig. 979, p. 272) and *antipyrine*, m.p. 70° (*Ph. C.* xxxiii. p. 714 ; *Ph. Ztg.* 1892, No. 94).

*Salicylic acid* has also been combined with *antipyrine* to form **salipyrine**, which had such a run during the influenza epidemic. Its structure is probably

FIG. 1236



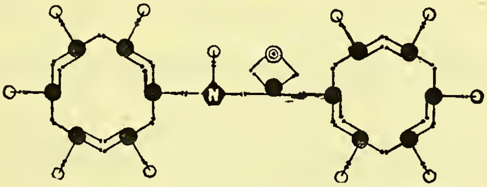
Salipyrine, antipyrine-salicylate, $C_{18}H_{18}N_2O_4$ ; m.p. 91°·5 ; antipyretic and antiseptic

**Antikamine** is a mixture of antipyrine, sodium-bi-carbonate, and traces of tartaric acid and caffeïne.

After this antipyrine episode we may finish the class by mentioning two more anilides.

One formed from *benzoic acid* and *aniline* :

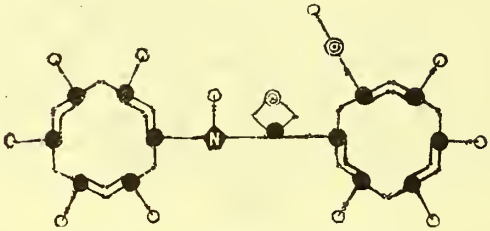
FIG. 1237



Benzanilide, $C_{13}H_{11}NO$ ; m.p. 158°; antipyretic

Another is formed from *salicylic acid* and *aniline*:

FIG. 1238



Salicylanilide, $C_{13}H_{11}NO_2$; m.p. 134°

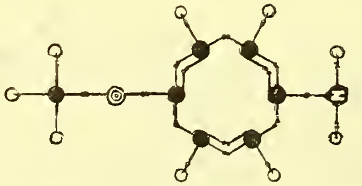
Salicyl-brom-anilide (*antinervine*) has nothing to do with this compound (*vide* p. 342).

## Amido-phenols (p. 321)

Although not in strict order, they have so much in common with amines that I have thought it right to refer to them here.

We have already mentioned one combination between amido-phenol and acetic acid (*vide* p. 342), in which a hydrogen in the amido-group was replaced. Another class of derivatives are analogous to the anilides, and differ from them chiefly in the capability of the phenol's hydroxyl of forming ethers. Thus amido-phenol will form an ether with *methyl-alcohol*, separating a molecule of water:

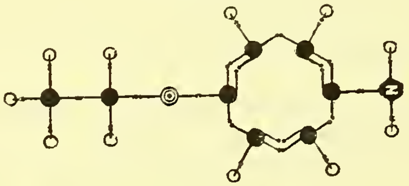
FIG. 1239



*p*-Anisidine, methyl-*p*-amido-phenate, $C_7H_9NO$; m.p. 56°

and with *ethyl-alcohol*:

FIG. 1240



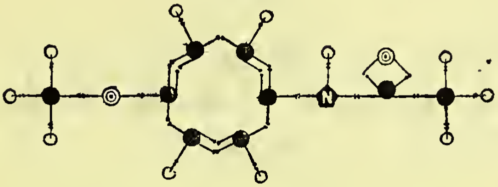
Phenetidine, ethyl-*p*-amido-phenate, $C_8H_{11}NO$; b.p. 253°; antifebrilium

Phenetidine may also be considered amido-phenetol (comp. fig. 495, p. 117).

These two compounds have through further substitutions enriched the modern materia medica with many remedies, good, bad, and indifferent. That is chiefly done by replacing a hydrogen-atom in the amido-group by the radical of an acid (p. 200).

Thus from *acetic acid* and *anisidine* is derived

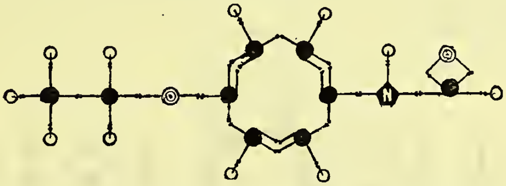
Fig. 1241



Methacetine, para-acet-anisidine, para-oxy-methyl-acetanilide, $C_9H_{11}NO_2$; antipyretic and analgesic

From *formic acid* and *phenetidine*:

Fig. 1242

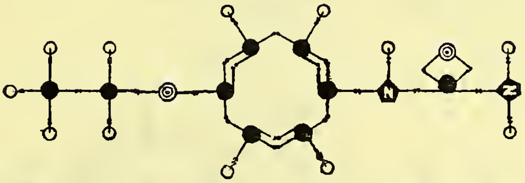


Formyl-para-amido-phenol-ether, formyl-phenetidine, $C_9H_{11}NO_2$; m.p. 62°; it has a powerful effect upon the spine; is said to be a safe antidote to strychnine, but has scarcely any antipyretic property

If the radical of valeric acid, mono-valent valeryl, is introduced instead of the formyl-group in the above structure, we obtain valeryl *p*-amido-phenetol, m.p. 350–360°, recently patented as sedatine, a sedative. (*Note.*—Antipyrine has also been called *sedatine.*)

By introducing an amido-group into the carbonyl-end of formyl-phenitidine it is turned into an amide:

Fig. 1243

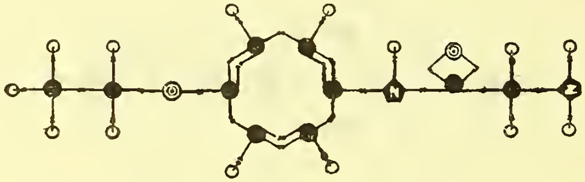


Dulcine, sucrol, para-phenetol-carbamide, $C_9H_{12}N_2O_2$; m.p. 160°

This may be also considered a combination of phenetol (fig. 495, p. 117) and urea (fig. 1174, p. 328; *vide* also p. 371). It has recently been started as an opposition compound to saccharine (fig. 1308, p. 368), because it is very sweet—about 200 times more so than sugar, still somewhat less than saccharine. It is not easily soluble in water, a saturated solution corresponding to about a 10-per-cent. sugar solution; but, on the other hand, it is credited with a pure sweet taste, which saccharine has not.

If a methylamine group is substituted for the amido-group, we get a combination of glycocoll (fig. 1156, p. 324) with amido-phenetol or phenetidine (fig. 1240, p. 346).

FIG. 1244

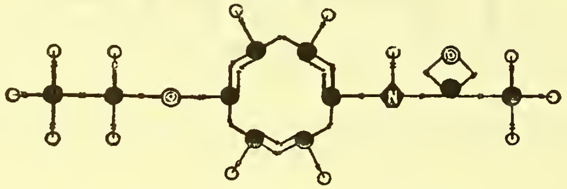


Phenocol, glycocoll-*p*-phenetidine, $C_{10}H_{14}N_2O_2$; m.p. 100°; antipyretic and antirheumatic, chiefly as hydrochloric salt

As salicylate, formed by introducing *salicylic acid* into the amido-group, it is termed salocol, a specific in influenza.

From *acetic acid* and *phenetidine*:

FIG. 1245

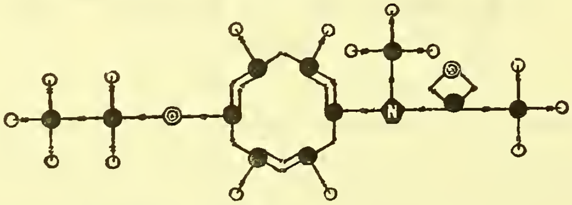


Phenacetine, acetophenetidine, ethoxy-acetanilide (in France, phenetidine), $C_{10}H_{13}NO_2$; m.p. 135°; febrifuge, antineuralgic and sedative

If acetyl in the figure is replaced by the mono-valent radical of lactic acid, the compound is termed lactophenine, said to be more soluble than phenacetine.

Affixing a *methyl* to the nitrogen in phenacetine we have

FIG. 1246

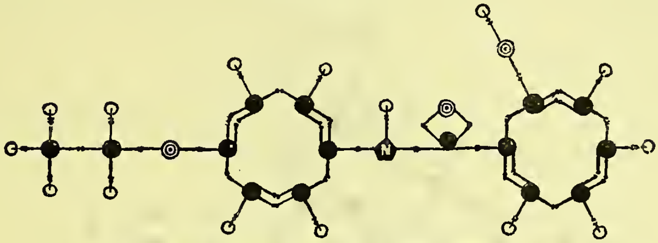


Methyl-phenacetine, $C_{11}H_{15}NO_2$; m.p. 40°

The properties of phenacetine are essentially changed by the introduction of the methyl-group; from being an antipyretic it appears as a hypnotic.

From *salicylic acid* and *phenetidine*:

FIG. 1247



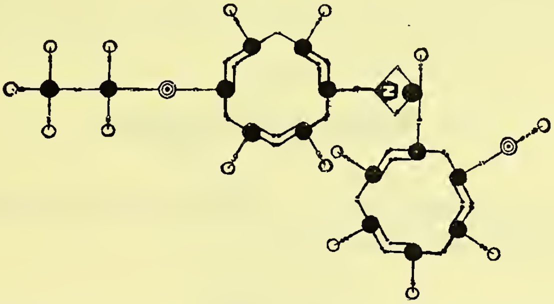
Saliphene, $C_{15}H_{15}NO_3$; m.p. 140°

not to be confounded with salophene (fig. 1229, p. 343).

From *salicylic aldehyde* and *phenetidine*.

Phenetidine combines with salicylic aldehyde (fig. 559, p. 135), the amido-group joining the carbonyl of the aldehyde through the elimination of a molecule of water in oxime style (comp. fig. 1073, p. 303). The compound which is a very 'new remedy' has been termed malakine.

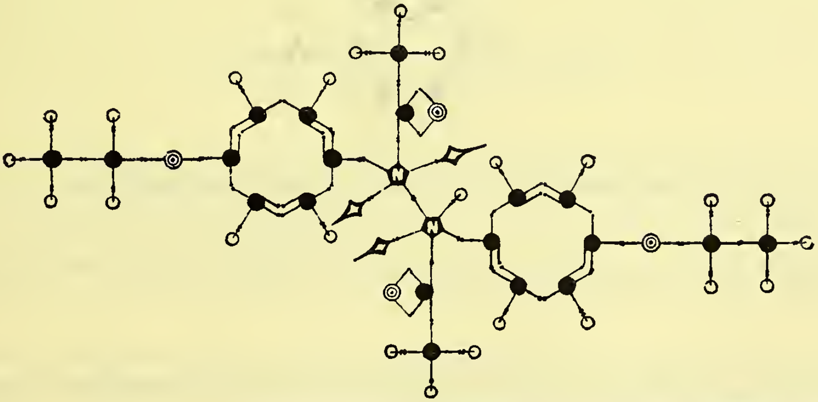
FIG. 1247 A



Malakine, salicyl-aldehyde-*p*-phenetidine, $C_{15}H_{15}NO_2$; m.p. 92°; mild but reliable antipyretic; also recommended in acute articular rheumatism and neuralgia (*Corresp. Bl. f. Schweiz. Aerzte*, 1893, p. 609; *Ph. C.* xxxiv. p. 598)

When iodine acts upon phenacetine three atoms of the former enter into two molecules of the latter, the whole being formed into one molecule: the triad nitrogens are at the same time changed into pentads:

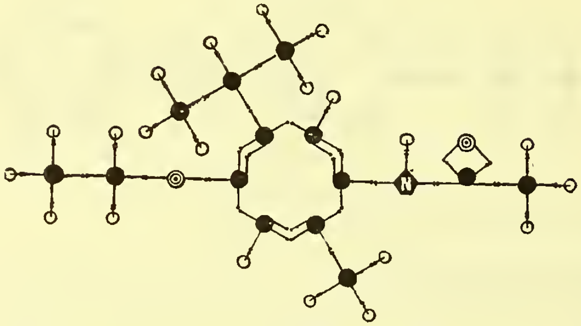
FIG. 1248



Iodophenine, $C_{20}H_{25}I_3N_2O_4$; m.p. (decomp.) 130°; bactericide, praised by some; abused by others

When phenol in phenacetine is replaced by thymol (fig. 434, p. 97) we have a compound of this structure:

Fig. 1249

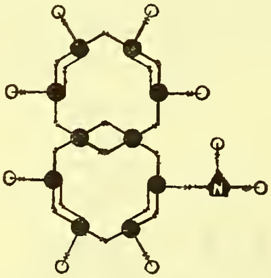


Thymacetine, $C_{14}H_{21}NO_2$; useful in nervous headache

## Amido-naphthalenes

Interlocked benzene-rings may also replace one of the hydrogens of ammonia. Thus naphthalene (fig. 159, p. 32) will form a primary amine:

Fig. 1250



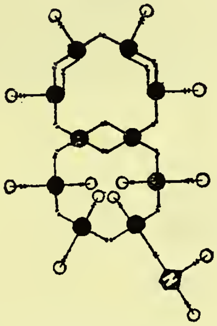
a-Naphthylamine, $C_{10}H_9N$; m.p. 50°; antiseptic and antidiphtheritic

*a*-Naphthylamine is employed in the manufacture of azo-dyes, and prepared on a large scale.

Sulphonic acid derivatives of naphthylamine are known in great numbers. One of them with sulphonic acid in para-position (1 : 4) to the amido-group is termed naphthionic acid, and is used in the preparation of dyes (*vide* Congo-dye, p. 337).

If to β-naphthylamine four hydrogen-atoms are added (hydrated) we obtain

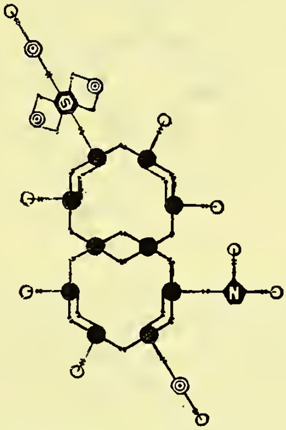
Fig. 1251



Thermine, tetrahydro-naphthylamine, $C_{10}H_{13}N$ ; b.p. 250° (710 mm.) ; mydriatic ; increases the temperature 4–5°

Similarly *β-naphthol* (fig. 452, p. 103), which sulphonated, forms with ammonia

Fig. 1252



Amido-β-naphthol-sulphonic acid, $C_{10}H_9NSO_4$

The sodium salt (sodium replaces hydrogen in sulphonic acid) is called eikonogen. In aqueous solution with sodium sulphite and soda or potash it is a powerful photographic developer (*vide* p. 357). Caustic alkalis in lieu of carbonates constitute the so-called 'rapid developers.' Sometimes potassium-ferrocyanide is added.

## DERIVATIVES FROM SECONDARY AMMONIA-BASES (*vide* p. 314)

There are but few of these compounds calling for our attention.

*Ethyl-aniline* (fig. 1119, p. 314) will form an interlocked pentagon and hexagon when we remove four hydrogens, three from the ethyl-end and one from the ortho-position:

Fig. 1253

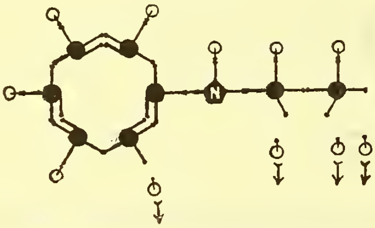


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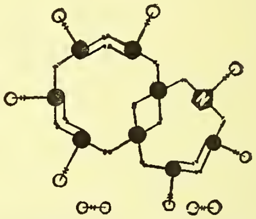
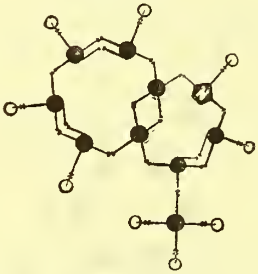
Fig. 1254



Ethyl aniline – four hydrogen-atoms = Indole, $C_8H_7N$; m.p. 52°

By introducing a *methyl* we obtain

Fig. 1255



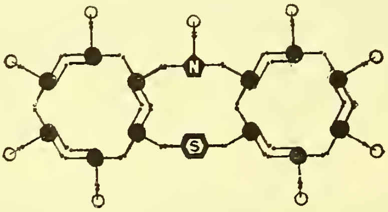
Skatole, β-methyl-indole, $C_9H_9N$; m.p. 95°

Indole and skatole are also produced by the pancreatic fermentation of albumen, and are therefore found in fæces, the odour of which is due to these two compounds.

Indole may be considered derived from a condensation of benzene and pyrrol (fig. 1182, p. 329). Compare also indene (fig. 147, p. 30), in which the imide is replaced by methylene.

The two phenyls in di-phenylamine (fig. 1117, p. 314) may be connected with a second bond through the intervention of sulphur, creating a thio-compound.

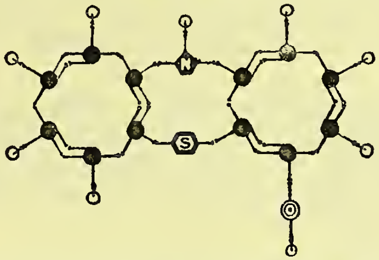
Fig. 1256



Thio-di-phenylamine, $C_{12}H_9NS$; yellowish plates; m.p. 180°; this structure may be looked upon as anthracene in which the ethane group has been replaced by groups from ammonia and sulphuretted hydrogen

By substituting hydroxyl for one of the hydrogen-atoms (ortho-position to sulphur) we obtain

Fig. 1257

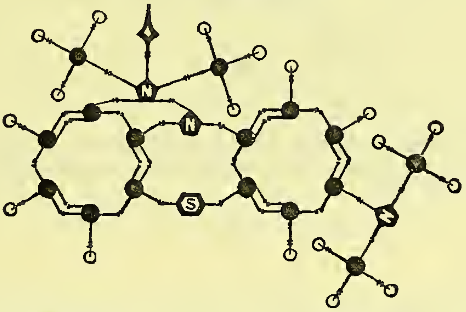


Sulphaminol, thio-hydroxy-di-phenylamine, $C_{12}H_9NSO$; m.p. 155°; antiseptic; when brought into contact with animal liquids it splits up, and both sulphur's and phenol's antiseptic properties come into play; it is said to be non-poisonous

Through the substitution by a *di-methylamine* in one of the phenyls, and a *di-methyl-ammonium chloride* in the other, we obtain methylene-blue.

The substitutions are more easily understood from the pictorial representation than from any amount of description:

Fig. 1258



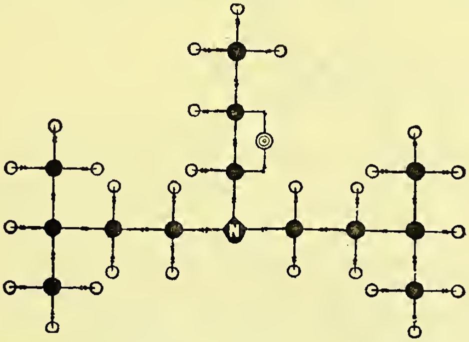
Methylene-blue, tetra-methyl-thionine-chloride, $C_{16}H_{18}N_3SCl$; blue scales; non-poisonous; antiseptic; used in malaria, tuberculosis, and gonorrhœa; analgesic in neuritic processes and rheumatic affections

Antirheumatinum is a combination of methylene-blue with sodium salicylate, antirheumatic.

## DERIVATIVES FROM TERTIARY AMMONIA-BASES (*vide* p. 315)

Of tertiary amines only one shall be added to those mentioned before on p. 315, viz.

Fig. 1259

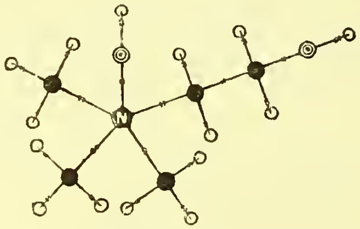


Oxy-propylene-di-iso-amyl-amine, $C_{13}H_{27}NO$; a liquid (*Ann.* [6], xiii. p. 433); acts as a heart-tonic and stimulant; given in large doses causes epileptic fits

## DERIVATIVES FROM QUARTERNARY AMMONIUM-BASES (*vide* p. 316)

We have several interesting compounds amongst quarternary ammonium-bases formed from tetra-methyl-ammonium hydroxide (fig. 1124, p. 316) by replacement of one of the methyls. When an alcohol enters as substitute, the compound is a quarternary hydramine (p. 321); thus if methyl is replaced by *hydroxy-ethyl* (fig. 391, p. 81), the radical of ethylene glycol (fig. 364, p. 76), we obtain **choline**:

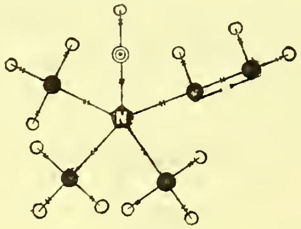
Fig. 1260



Choline, hydroxy-ethyl-tri-methyl-ammonium-hydroxide, bilineurine, sinkaline, $C_5H_{15}NO_2$; syrupy fluid, decomposing when heated; is a decomposition product of lecithin, and appears as such in the animal organism, specially when life is extinct; has been used in diphtheria

When a molecule of water is split off from the hydroxy-ethyl of choline, we obtain **neurine**, a base of the following structure:

Fig. 1261

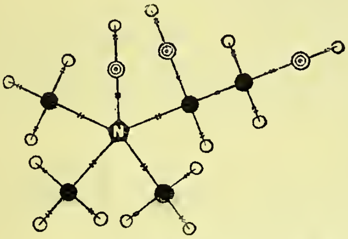


Neurine, vinyl-tri-methyl-ammonium-hydroxide, $C_5H_{13}NO$; very poisonous

The free base is only known in aqueous solution. Is found in dead bodies together with choline, from which it is probably formed—as soon as choline is separated from lecithin—as a product of decomposition, very likely through the action of micro-organisms (*Arch. d. Ph.* xci. p. 76).

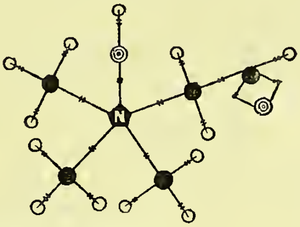
By the exposure of choline to oxidising agents, another hydroxyl may replace a hydrogen in the hydroxy-ethyl-group, producing a new, very poisonous, compound from choline; the opinions about its structure are, however, not unanimous, some believing that the alcohol-group has been oxidised to an aldehyde-group:

Fig. 1262



or

Fig. 1263

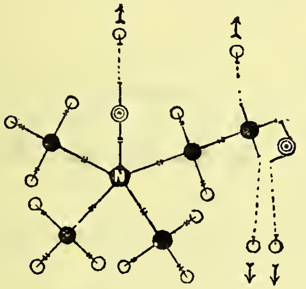


Muscarine, $C_5H_{15}NO_3$ or $C_5H_{13}NO_2$; deliquescent crystals

The difference of the two empirical formulæ being $H_2O$, the latter structure supposes a molecule of water being present as water of crystallisation; muscarine is not poisonous to flies. Occurs in a toadstool, *Agaricus muscarius*, where another poisonous compound is also present, which is an antidote to muscarine; hence the toadstool is often eaten without injury. Atropine is also an antidote.

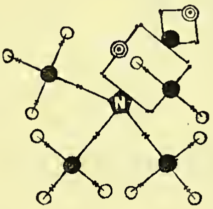
Choline may also be oxidised in a third way: by the first oxidation (to neurine) one oxygen and two hydrogen-atoms were removed from the hydroxy-ethyl-group; by the second oxidation (to muscarine) two hydrogen-atoms were removed, one of them belonging to the hydroxyl (or, according to the alternate view, a hydroxyl was introduced); by a third and more energetic way, and probably through the usual but momentary stages of aldehyde and acid, a lactone, betaïne, is formed, whose structure is perfectly analogous to the one suggested for amido-acids (fig. 1157, p. 324), and the formation of which directly from choline may be thus represented:

Fig. 1264



Choline less two molecules of hydrogen

Fig. 1265



Betaïne, tri-methyl-glycocoll, oxy-neurine, $C_5H_{11}NO_2$; deliquescent crystals; non-poisonous; occurs in beet root and other plants, also in bivalves

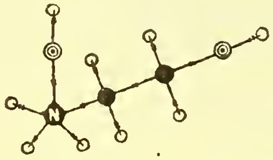
It will be remembered that the triad ammonia united with acids in a rather peculiar way, its nitrogen, turned into a pentad by the presence of the acid, seizes with one of the two new valencies the carboxyl's hydrogen, and with the other the rest of the acid (*vide* p. 323); further, that the nitrogen in amido-acetic acid was influenced in the same way by its own acid-constituent (*vide* p. 324). We have also seen above that betaïne is supposed to have a structure analogous to that of glycocoll; consequently we are justified in presuming that betaïne is an amido-acid, the structure of which it will assume in its derivatives; on the other hand we know that betaïne is derived from a hydroxy-ammonium-alcohol, and have, therefore, some reason to conclude that glycocoll, sarcosine, &c., are derivable from corresponding but as yet unknown compounds. It would be interesting from a physiological point of view also, to verify this, because they are all products of katabolic processes in the organism. I therefore give below parallel illustrations of glycocoll, sarcosine, and betaïne, their derivations and their derivatives:

Derivation

Betaïnes

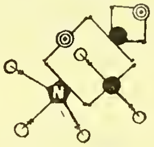
Structure in Derivatives

Fig. 1265 a



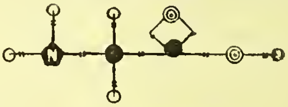
Hydroxy-ethylium-hydrate; hypothetical

Fig. 1265 b



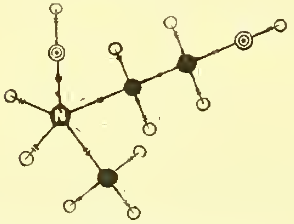
Glycocoll

Fig. 1265 c



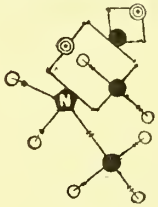
Amido-acetic acid

Fig. 1265 d



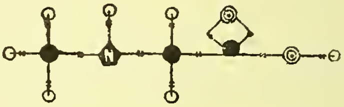
Methyl-hydroxy-ethylium-hydrate;
hypothetical

Fig. 1265 e



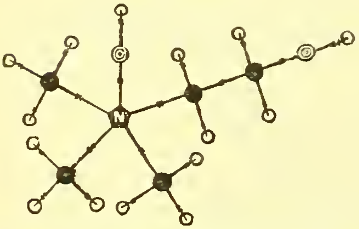
Sarcosine

Fig. 1265 f



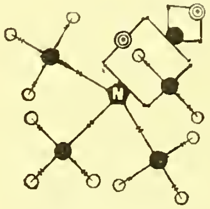
Methyl-amido-acetic acid

Fig. 1265 g



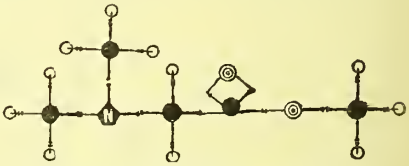
Tri-methyl-hydroxy-ethylium-hydrate,
choline

Fig. 1265 h



Betaïne

Fig. 1265 i

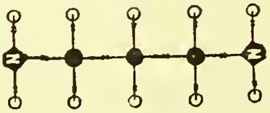


Di-methyl-amido-acetic methyl-ether

## DIAMINES AND THEIR DERIVATIVES (*vide* p. 317)

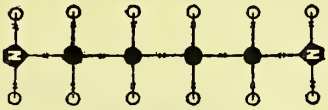
This group includes many important and interesting compounds. We have already (p. 317) represented ethylene-diamine. We have further

Fig. 1266



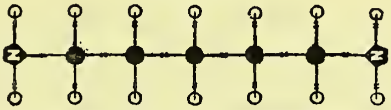
Tri-methylene diamine, $C_3H_{10}N_2$; b.p. 135° (738 mm. pressure)

Fig. 1267



Tetra-methylene-diamine, putrescine, $C_4H_{12}N_2$; m.p. 24°, b.p. 156°; poisonous; smells like sperma; occurs in putrid meat, glue, corpses; also in urine and fæces in cystin-uria

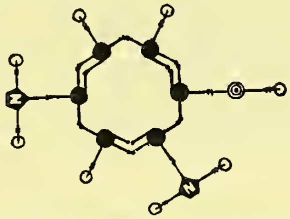
Fig. 1268



Penta-methylene-diamine, cadaverine, $C_5H_{14}N_2$; b.p. 175°; poisonous; has an odour of tetra-methylene-diamine, together with which it generally occurs in nature

Neuridine is an isomer; its structure is, however, not known. It occurs in putrid meat and fish, smells disgustingly, but is not poisonous.

Fig. 1269



Di-amido-phenol, $C_6H_8N_2O$; is easily decomposed; photographic developer

Photographic developers. The photographic process, as is well known, consists in exposing finely divided halogen compounds of silver to the light. Although to all outward appearances the silver compound has undergone no change by the exposure, still the connection between the atoms has been loosened by the influence of the rays of light, and this loosening is quantitatively proportionate to the amount of actinic (chemically active) rays. When a reducing agent is allowed to act upon these light-affected molecules, it combines with the halogen-atoms thus loosened, but it has not sufficient power to separate the molecules of those silver halogens upon which no light has been thrown. The *fixing* consists in the application of a compound that will dissolve the silver halogens, but leave the reduced silver alone. Formerly ferrous sulphate and oxalate were much used as reducing agents, but the development of organic chemistry of late years has brought to light compounds which are better adapted for the purpose. We have already had occasion to mention several of them: catechol, hydroquinone, pyrogallic acid (pp. 92, 93), *p*-amido-phenol (p. 321), di-amido-benzene (fig. 1126, p. 317), &c. Now it is rather interesting to notice that all these belong to the aromatic series, and that they have at least two hydroxyls, or two amido-groups, or one of each of these introduced into the ring; further, that these two substitutes are either in ortho- or para-position, never in meta-position, except when either of the two other positions pre-exists (pyrogallic acid). Such two groups are indispensable to a developer; any substitution in them destroys their ability to develop (Society of Chemical Industry, meeting December 7, 1891).

Amidol, a developer, is a solution of di-amido-phenol and sodium sulphite (*Ph. C.* xxxiii. p. 486).

Rodinal, another developer, is a solution in one litre water of para-amido-phenol (fig. 1144,

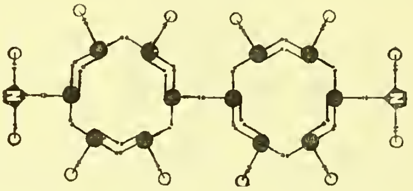
p. 321) five grammes, sodium-sulphite fifty grammes, and potassium-carbonate twenty-five grammes (*Amateur Photograph*, 1891, p. 180).

Eikonogen (*vide* fig. 1252, p. 351).

Metol is *p*-amido-*m*-cresol.

There is one more diamine to mention, derived from di-phenyl (fig. 296, p. 57).

Fig. 1270

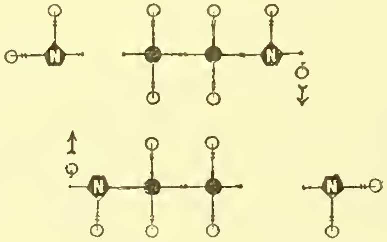


*p*-Di-amido-di-phenyl, benzidine, $C_{12}H_{12}N_2$; m.p. 122°

Benzidine is an important compound in the colour industry, forming the mother substance of the so-called cotton-dyes which dye cotton without any mordant (substantive colours), amongst them being the Congo-dye (*vide* fig. 1215, p. 337).

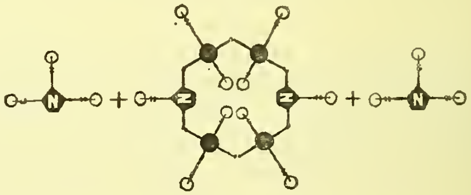
There are, however, several important and interesting compounds which may be looked upon as derivatives of diamines. Thus, when we remove two molecules of ammonia from two molecules of ethylene-diamine, the rest will join, forming one molecule:

Fig. 1271



Two molecules of ethylene-diamine – two molecules of ammonia

Fig. 1272



Two molecules of ammonia + piperazine, piperazidine, di-ethylene-di-amine, $C_4H_{10}N_2$; m.p. 105°

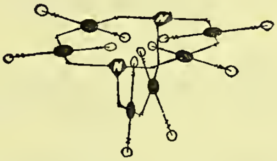
Piperazine is the best solvent for uric acid, and therefore used in most of the diseases which the presence of that compound gives rise to

Piperazine is hydrated pyrazine (*vide* fig. 1402, p. 389).

Spermine, a rather mystic individual, said by some to be contained in the testicles (pooh-poohed from other quarters), was at one time considered identical with di-ethylene-di-amine, but later acknowledged to be, if anything, an isomer or polymer. Its simplest empirical formula has been stated to be $C_2H_5N$, which, however, according to the latest information (*Ber.* xxiv. p. 359), has now been altered to $C_{30}H_{26}N$. Alleged to be adorned with rather attractive properties, especially to old gentlemen, it has the suspicion about it of being put on the market 'on spec.'

Another similar derivative is tri-ethylene-di-amine, formed from three *ethylene-di-amines* splitting off four ammonias. It is impossible to represent its structure geometrically, if the length of the valencies are to be reasonably preserved. I shall therefore give a stereometrical, or rather perspective, drawing of it:

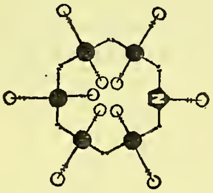
Fig. 1273



Tri-ethylene di-amine, $C_6H_{12}N_2$; b.p. 170°

When an *ammonia* is split off from *penta-methylene-diamine* (fig. 1268, p. 357) the chain will close, as there will be two free valencies, one at each end:

Fig. 1274

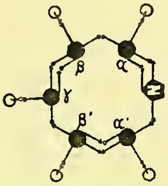


Piperidine, $C_5H_{11}N$; b.p. 106°; has an odour resembling that of pepper

Such cyclo-compounds derived from amines by transformation of amido- into imido-groups are distinguished also as *imines*; those with one imido-group are termed *monimines*, e.g. piperidine; those with two, *diimines*, e.g. piperazine; and those with three, *triimines*, e.g. triethylene-triamine (fig. 1128, p. 317).

If we remove the five hydrogen-atoms inside the ring, and the one attached to nitrogen, we obtain a hexagon with double bonds in benzene style:

Fig. 1275



Pyridine, $C_5H_5N$; b.p. 114°

Pyridine is obtained from tar; used as an inhalation for asthma, and for mixing with alcohol, in order to render it undrinkable, in countries where spirit for technical use is exempt from taxation (denaturated spirit). It is also a disinfectant and an antiseptic.

From piperidine and pyridine many important compounds are derivable. It would too much interrupt the course of our ammonia-compounds to mention them here; we shall therefore discuss them afterwards under one head, together with similar and allied compounds.

## POLY-AMINES AND THEIR DERIVATIVES (*vide* p. 317)

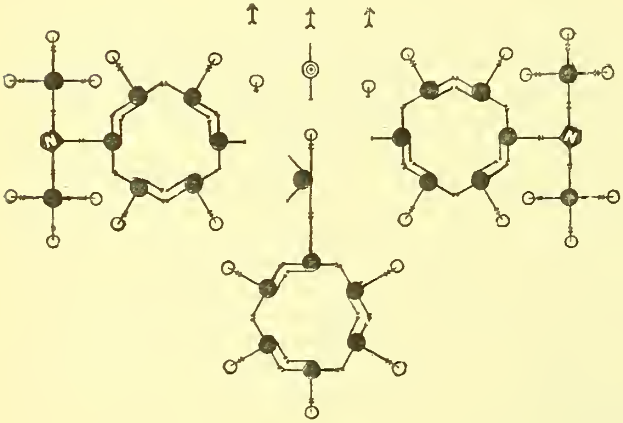
As far as therapeutics are concerned, there is not much to interest us in this class, but all the so-called aniline dyes have their place here, and it may perhaps be of interest to look a little at their constitution.

They are all derived from tri-phenyl-methane (fig. 251, p. 47), which is the starting-point in the preparation of four groups of dyes: 1. Malachite-green-group. 2. Rosaniline-group. 3. Rosolic acid-group. 4. Phthaleïne-group. The structures of the two latter have already been explained (pp. 108, 224). The malachite-green-group belongs to di-amines, but as it is so nearly related to rosaniline-compounds, which are tri-amido-derivatives, their discussion has been deferred until now in order to treat them in succession.

The amido-derivatives of tri-phenyl-methane are colourless compounds (leuco-compounds), their salts being the proper dyes.

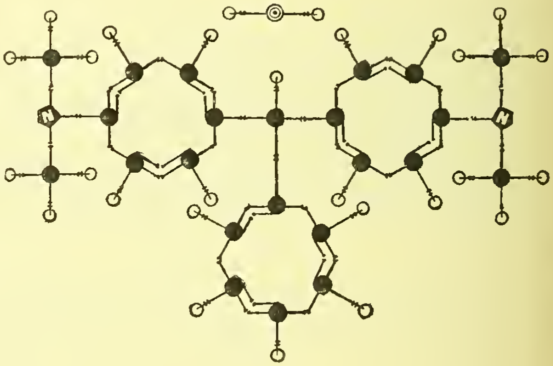
Malachite-green, bitter-almond-oil-green. The basis of this dye is tetra-methyl-di-amido-tri-phenyl-methane, formed from one molecule of bitter-almond-oil (fig. 554, p. 134) and two molecules of di-methyl-aniline:

Fig. 1276



Di-methyl-aniline Bitter-almond-oil Di-methyl-aniline =

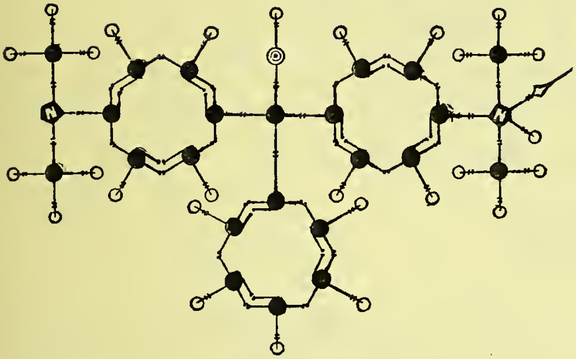
Fig. 1277



Tetra-methyl-di-amido-tri-phenyl-methane, leuco-malachite-green, $C_{23}H_{26}N_2$; m.p. 93°

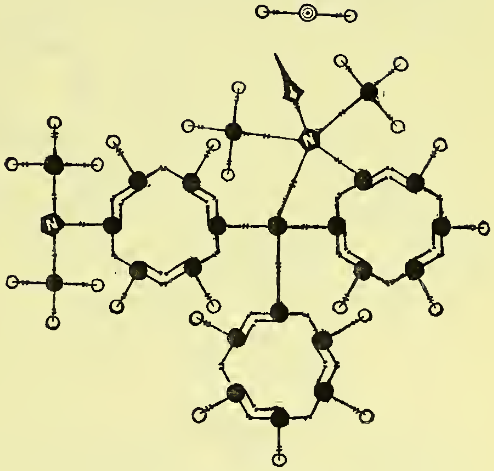
Into this leuco-base a hydroxyl is introduced by oxidation; it is then dissolved in cold hydrochloric acid, forming the chloride salt which is still colourless until warmed, when an intensely green colouration of the solution is produced by the chlor-ammonium-group jumping from para- to ortho-position (intramolecular change), exchanging places with the hydrogen, and joining the methane-group by dropping a molecule of water.

Fig. 1278



Tetra-methyl-di-amido-tri-phenyl-carbinol-chloride

Fig. 1279



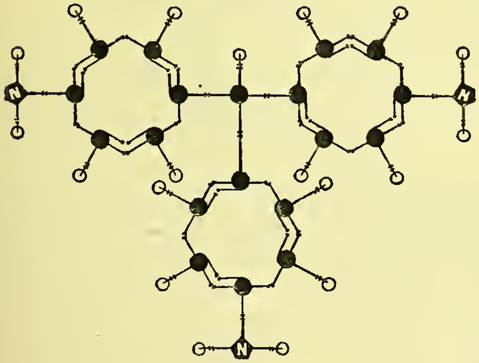
Malachite-green

By exchanging methyls for ethyls, by introducing more chlorine or sulphur-groups, &c., a variety of green dyes are produced, such as Brilliant-green, Victoria-green, Helvetia-green, &c.

Rosaniline is a tri-amido compound, also derived from *tri-phenyl-methane.* This tri-amido tri-phenyl-methane is termed para-leucaniline; when a hydroxyl through oxidation has been introduced into its methane-group it is called para-rosaniline; and, further, if a methyl-group has replaced a meta-hydrogen in one of the phenyls, its name is rosaniline.

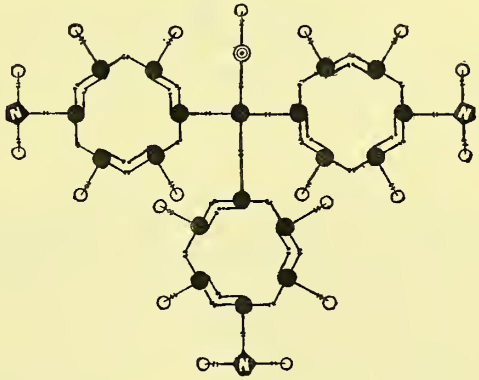
Their mutual relations will be seen from their structures:

Fig. 1280



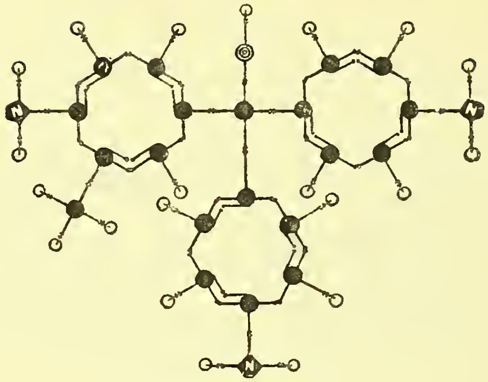
Para-leucaniline, $C_{19}H_{19}N_3$; m.p. 148°

Fig. 1281



Para-rosaniline, $C_{19}H_{19}N_3O$

Fig. 1282



Rosaniline, $C_{20}H_{21}N_3O$

None of these (leuco-compounds) are dyes yet; in order to make them such, it is necessary to turn them into salts by combining them with an acid, generally hydrochloric acid; they are then real dyes, and termed para-fuchsines or fuchsines, according to their derivation.

Hydrochloric acid joins the oxidised leuco-base through addition, i.e. it occupies two of the latent valencies in one of the amido-groups, and the newly-formed ammonium-group exchanges places with an ortho-hydrogen, just as was the case in malachite-green, but this time warming is unnecessary.

Fig. 1283

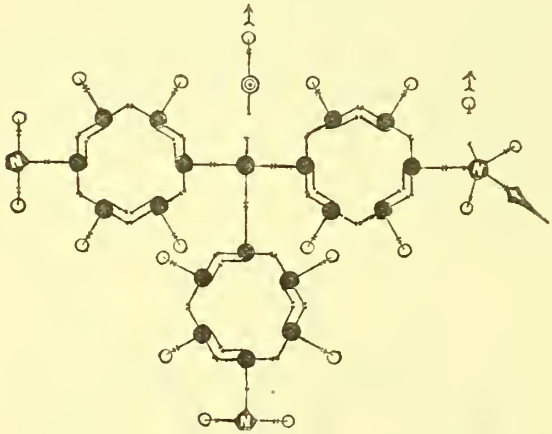
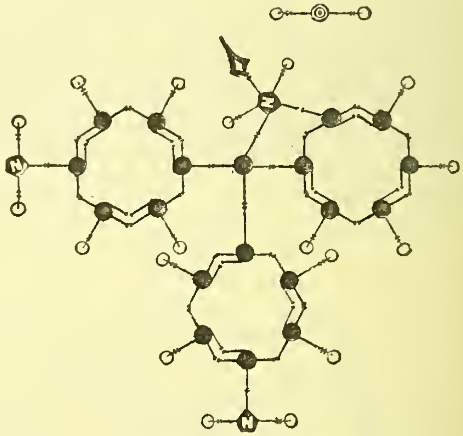


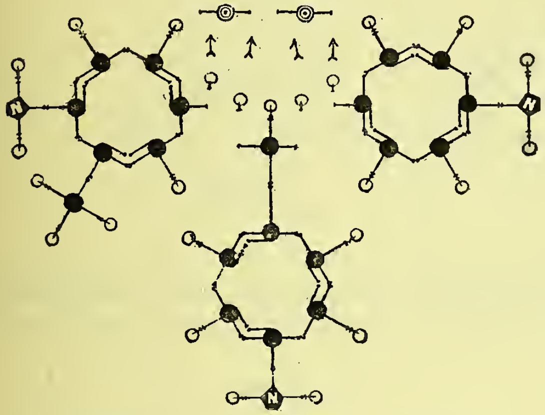
Fig. 1284



Para-fuchsine, $C_{19}H_{18}N_3Cl$

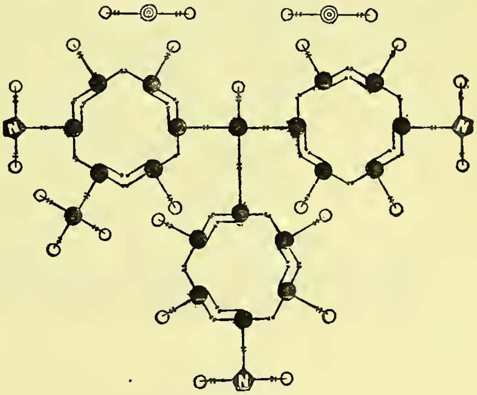
The practical production of chemical compounds is very often different from the theoretical derivation; it was so in forming malachite-green, and so it is in this case. The manufacturers do not start from tri-phenyl-methane; they take for their starting-point the crude benzene, that part of the coal-tar that distils at 80–90°, mainly consisting of benzene, toluene, and a few higher homologues. These compounds are first nitrated and then reduced, the end-products being amido-compounds of the different hydrocarbons (*vide* p. 335). The boiling-point of this mixture varies according to the relative proportion of amido-compounds; a low boiling-point indicates more benzene-compounds and less of the higher homologues, whereas with a benzene of high boiling-point the case is reversed. Thus it is possible to control the composition of the mixture which is to be treated, and, *e.g.*, for the production of rosaniline a mixture is selected which contains about a molecule each of aniline, ortho- and para-toluidine. Through the action of oxygen four of their hydrogen-atoms are removed, and the three molecules join, forming leucaniline. This process will be easily understood from the following representation :

Fig. 1285



*o*-Toluidine *p*-Toluidine Aniline

Fig. 1286



Leucaniline

Further oxidation introduces the hydroxyl and turns it into rosaniline. Arsenic acid was formerly employed as the oxidising agent, but nitrobenzene is now more used.

As mentioned, *hydrochloric acid* is perhaps most frequently used for forming the salt, but others are also employed, such as *nitric*, *sulphuric*, *acetic*, *picric*, and *tannic acids*. A great number of derivatives are arrived at by substitutions of the amido-hydrogens (of which there are six), by *methyl*, *ethyl*, *phenyl*, *tolyl*, *sulpho-groups*, &c., turning the red colour of fuchsine into different shades of blue and green.

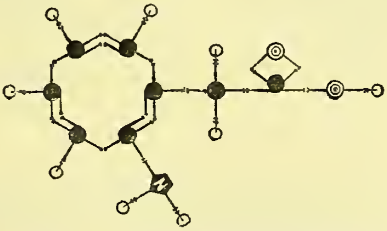
Methyl-violet is a mixture of tetra-, penta-, and hexa-methyl-para-rosaniline. Crystal-violet is the pure hexa-methyl compound. The methyl-violets are antiseptics, and have been used as such both externally and internally.

Pyoktannin is also a mixture of different methyl-para-rosanilines, probably the tannates. It has been employed in cancer, diphtheria, gonorrhœa, laryngeal tuberculosis, and otorrhœa.

## AMIDO-ACIDS AND THEIR DERIVATIVES (*vide* p. 324)

Some more amido-acids having their amido-group in ortho-position are of interest on account of the interlocked rings they so easily form. Thus we have from *phenyl-acetic acid* (fig. 813, p. 212), with amido in ortho-position :

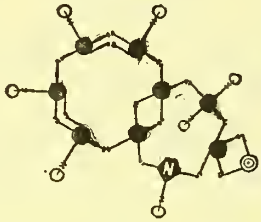
Fig. 1287



*o*-Amido-phenyl-acetic acid, $C_8H_9NO_2$

It does not exist in the free state, but drops, in the usual way, a molecule of water formed from the hydroxyl and one of amido's hydrogens, the two free valencies caused by this separation of water joining:

Fig. 1288



Oxindole, $C_8H_7NO$; m.p. 120°

From *mandelic acid* (fig. 816, p. 213) we have ortho-amido-mandelic acid, which immediately separates a molecule of water and passes into its anhydride, di-oxindole, analogous to the above:

Fig. 1289

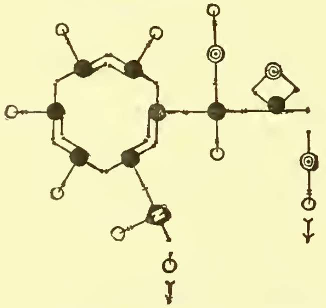


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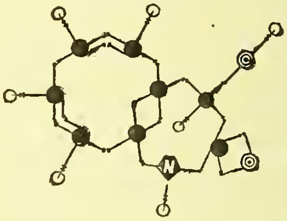
Fig. 1290



Ortho-amido mandelic acid = Di-oxindole, $C_8H_7NO_2$; m.p. 180°

From *benzoyl-formic acid* (fig. 817, p. 213) we have an ortho-amido-acid, which is somewhat more stable than the foregoing acids; still, when heated, this one, too, will drop a molecule of water:

Fig. 1291

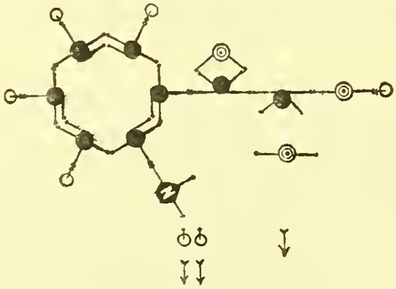


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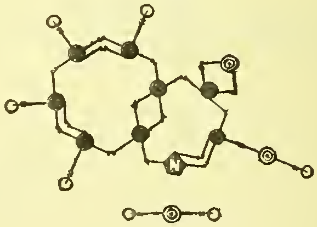
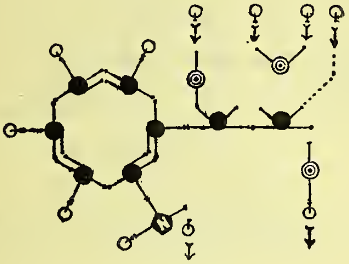
Fig. 1292



Ortho-amido-benzoyl-formic acid, isatic acid, $C_8H_7NO_3$; on being heated loses a molecule of water = Isatin, $C_8H_5NO_2$; m.p. 200°

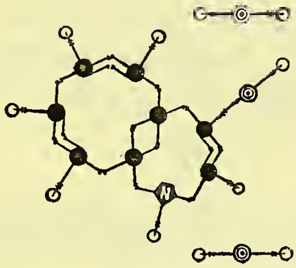
If *hydroxyl* also is removed from isatic acid through reducing agents (two molecules of hydrogen), the pentagon will have a different arrangement:

Fig. 1293



Isatic acid

Fig. 1294

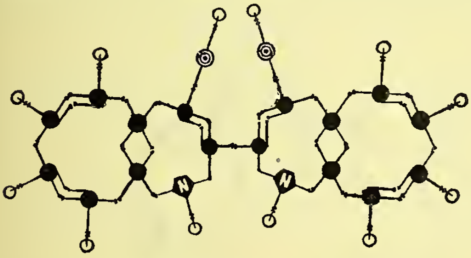


Indoxyl, $C_8H_7NO$; a brown oil, decomp. on heating

Indene (fig. 147, p. 30), indole (fig. 1254, p. 352), skatole (fig. 1255, p. 352), oxindole, di-oxindole, isatin, and indoxyl are nearly related, and easily converted into one another by reduction or oxidation. Their formation is somewhat similar to that of lactones (p. 182), wherefore these and similar compounds have been termed lactames when the amido-group has lost *one* hydrogen in the formation, and lactimes when *both* hydrogen-atoms are gone. Isatin is thus a lactime, the others lactames.

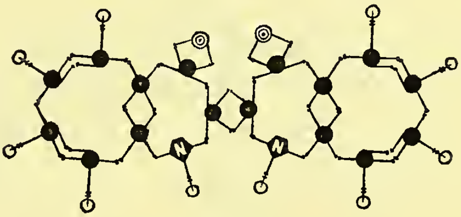
All of them may be derived also from indigo, and indigo may be derived from them. Thus two molecules of indoxyl unite by removing two hydrogen-atoms, and this compound, indigo-white, yields on oxidation indigo, two more hydrogen-atoms (from the hydroxyls) being removed, and the single bond between the two indoxyls being converted into a double one, the existing double bond in the pentagon breaking up.

Fig. 1295



Indigo-white, hydrindigotin, $C_{16}H_{12}N_2O_2$

Fig. 1296



Indigo, $C_{16}H_{10}N_2O_2$

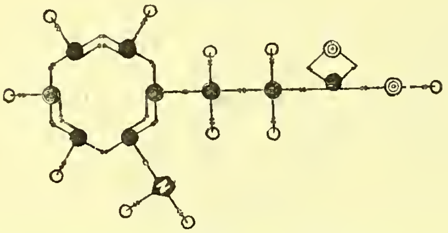
For another formation of indigo see p. 309.

Indigo-white may be considered the leuco-base (p. 360) of indigo.

We have further of similar amido-acids forming interlocked rings:

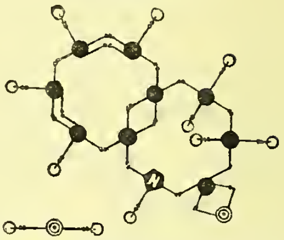
From *hydro-cinnamic acid* (fig. 814, p. 212):

FIG. 1297



*o*-Amido-hydrocinnamic acid, $C_9H_{11}NO_2$; unstable compound; goes immediately, by separation of the elements of water, into its lactame

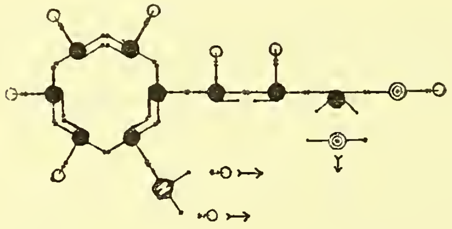
FIG. 1298



Hydrocarbostyril, $C_9H_9NO$; m.p. 160°

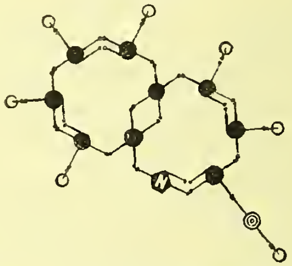
From *cinnamic acid* (fig. 821, p. 214), through lactime formation:

FIG. 1299



*o*-Amido-cinnamic acid, $C_9H_9NO_2$; m.p. 158°; goes into its lactime

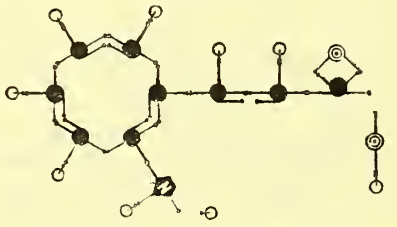
FIG. 1300



Carbostyril, α-hydroxy-quinoline, $C_9H_7NO$; m.p. 200°

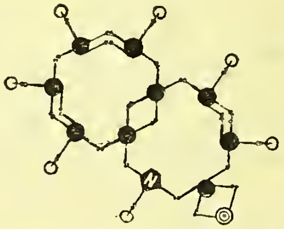
Some of carbostyril's reactions seem to indicate the structure of a *lactame*, formed from the same *o*-amido-cinnamic acid in a different way of water-formation (see lactame and lactime formation, p. 365):

FIG. 1301



o-Amido-cinnamic acid – a molecule of water

FIG. 1302



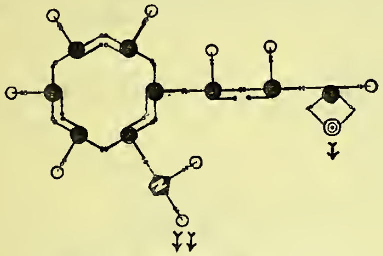
Pseudo-carbostyril, $C_9H_7NO$

Pseudo-carbostyril is also derivable from *hydro-carbostyril* by removing the two hydrogen-atoms inside the interlocked hexagon, a double bond being thereby formed.

This capability of assuming two forms (*tautomerism*) has met us before; phloroglucin (figs. 422, 424, p. 93) is especially analogous.

Carbostyril and hydro-carbostyril are, as the figures indicate, nearly related; they may be considered, together with numerous other compounds, derivatives from a common mother substance, quinoline, which, again, is derivable from o-*amido-cinnamic aldehyde* (*vide* cinnamic aldehyde, fig. 555, p. 134).

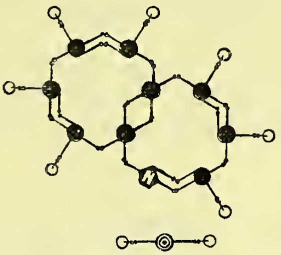
Fig. 1303



o-Amido-cinnamic aldehyde, $C_9H_9NO$
— a molecule of water

=

Fig. 1304

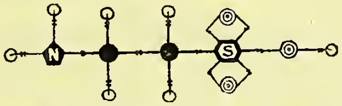


Quinoline, leucoline, $C_9H_7N$; b.p. 236°;
used as an antifebrile

There are still to be mentioned two or three amido-acids, in which sulphonyl, the radical of sulphonic acid (fig. 1037, p. 290), has been introduced.

If we in *β-amido-propionic acid* (p. 325) substitute *sulphonyl* for carboxyl, or in *ethyl sulphonic acid* (fig. 1040, p. 291) replace an alkyl-hydrogen in ethyl, or the alkyl-hydroxyl in *isethionic acid* (fig. 1043, p. 291) by an *amido-group*, taurine is formed:

Fig. 1305

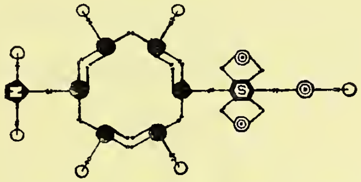


Taurine, amido-ethane-sulphonic acid, $C_2H_7SO_3$; decomp. at 240°; occurs in the bile

The bile contains the sodium salts of glycocholic acid and taurocholic acid. They are both combinations of cholic acid ($C_{24}H_{40}O_5$), the former with glycocoll, the latter with taurine. Besides these two acids, the bile contains choleïc acid ($C_{25}H_{42}O_4$) and fellinic acid ($C_{23}H_{40}O_4$), but the structure of neither these nor of cholic acid is understood.

Instead of an open chain of hydrocarbons between the amido- and sulphonyl-groups, as in taurine, a closed chain may be inserted; for instance, *benzene*, thus:

Fig. 1306



Para-amido-benzene-sulphonic acid, sulphanilic acid, $C_6H_7NSO_3$; decomp. on heating

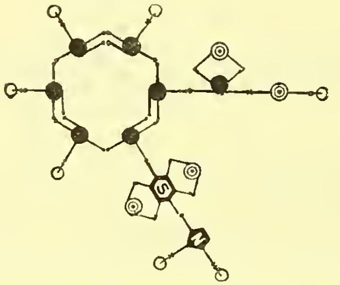
It may be looked upon as aniline combined with sulphuric acid by elimination of a molecule of water, which it, indeed, practically is. But though it combines with bases it does not combine with acids, which it ought to do if an amido-group is present; it has, therefore, been conjectured that it forms a salt itself with its acid and basic group bending towards each other; in that case the nitrogen would stretch out two more valencies turning from a triad into a pentad. One of these valencies would tear away the hydrogen from hydroxyl, oxygen's free valency thus created would be seized by nitrogen's other valency; in fact, it would be a sort of ammonium-phenyl-sulphonate. This way of linking could be represented only by a structure similar to fig. 1273, p. 359, the loop hanging down consisting in this case of ammonium sulphonate, whereas the joining of the amido- and sulphonic-groups is entirely analogous to that of glycocoll, illustrated in fig. 1157, p. 324.

Sulphanilic acid has been recommended in iodine-intoxication (*Monatsh. f. prak. Dermat.* 1893, p. 102).

The ortho- and meta-compounds have also been prepared.

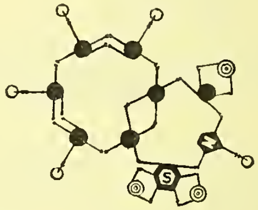
From *o*-sulpho-benzoic acid (fig. 1053, p. 295) an amido-acid may be formed; on account of the ortho-position it goes easily into the anhydride (lactame):

Fig. 1307



Ortho-sulphamido-benzoic acid, $C_7H_7NSO_4$; m.p. about 160°; has no sweet taste

Fig. 1308



Saccharine, benzoyl-sulphimide, $C_7H_5NSO_3$; m.p. 220°; exceedingly sweet, about 500 times more so than sugar; antiseptic

The two isomeric acids with the sulpho-amido-group in meta- or para-position are known; they are not sweet, and are found in commercial saccharine to the extent of 40 to 50 per cent., lowering proportionally the sweetness. According to *Ph. C.* xxxiv. p. 339, the pure ortho-compound is now in the market, either as such or as the more soluble sodium salt.

There is another, but bitter, saccharin, the lactone of saccharinic acid (fig. 701, p. 182), belonging to the aliphatic series.

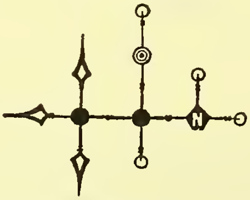
Odol is a perfumed alcoholic solution of salol and saccharine, antiseptic.

## DERIVATIVES FROM AMIDES AND ACID AMIDES (AMINIC ACIDS, p. 327)

There are a few combinations of chloralhydrate (fig. 977, p. 272) which have to be noticed. One or two of them do not belong to the amides, but on account of their close relation they are better mentioned together.

One is a combination of *chloralhydrate* and *ammonia* by separation of a molecule of water, and belongs to aldehyde ammonias, p. 322.

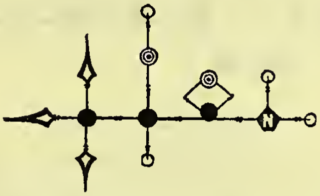
Fig. 1309



Chloral-ammonia, trichlor-ethidene-hydroxy-amine, $C_2H_4Cl_3NO$; m.p. 62°; hypnotic and analgesic, in lieu of urethane and chloralhydrate

Another is from *formamide* (fig. 1170, p. 327), and is a proper amide, if looked upon as formed from trichloro-lactic acid and ammonia :

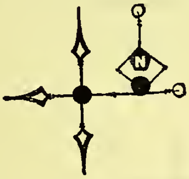
FIG. 1310



Chloral-amide, chloral-formamide, $C_3H_4Cl_3NO_2$ ; m.p. 114° ; hypnotic

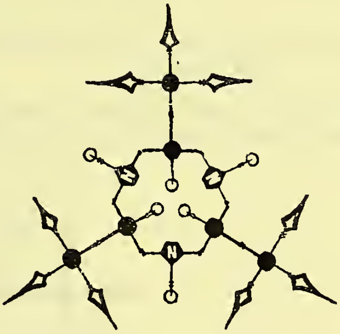
In yet another, the nitrogen of ammonia replaces the oxygen in the carbonyl of chloral, as we have already seen instances of before (benz-hydroxamic acid, fig. 1132, p. 318, hydrazones and osazones, p. 338), which makes it an imido-compound. Some chemists contend that a polymerisation takes place analogous to paraldehyde (fig. 540, p. 131) ; it has therefore either one or the other of these structures :

FIG. 1311



$C_2H_2Cl_3N$

FIG. 1312



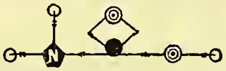
$C_6H_6Cl_9N_3$

Chloralimide ; m.p. 166° ; hypnotic, analgesic, and antipyretic

The only other compounds, which it is necessary to discuss as belonging to this class, are the derivatives from carbonic acid ; they, however, are both numerous and important, though we can here only single out the best, as far as we are concerned.

Carbonic acid is a di-basic acid, and as such may have either one or both of its carboxyl-hydroxyls replaced by amido-groups or substituted amido-groups, forming either amides or acid amides (aminic acids). We shall first discuss the derivatives from the compound formed by replacing one of the hydroxyls, viz. carbamic acid, which was thus represented (fig. 1173, p. 328):

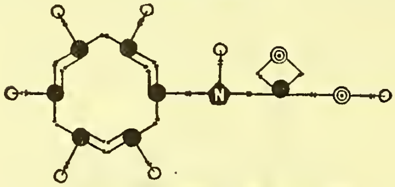
FIG. 1313



Carbamic acid, $CH_3NO_2$

Carbamic acid can have one hydrogen in the amido-group substituted by phenyl:

Fig. 1314

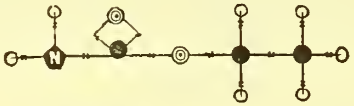


Carbanilic acid, $C_7H_7NO_2$

which may also be looked upon as a combination of *aniline* (fig. 1111, p. 313) and *carbonic acid*, and is therefore, together with urea and their derivatives, often classified as anilides of carbonic acid. Comp. p. 341.

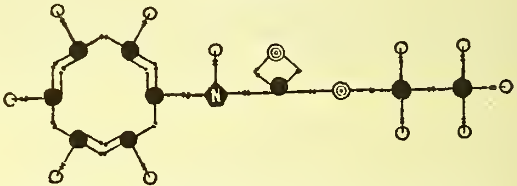
Neither of the two acids exists in the free state, but they can both form compound-ethers in great numbers; we shall mention the ethyl-ethers only:

Fig. 1315



Ethyl-carbamic ether, urethane, $C_3H_7NO_2$; m.p. 50°; mild hypnotic

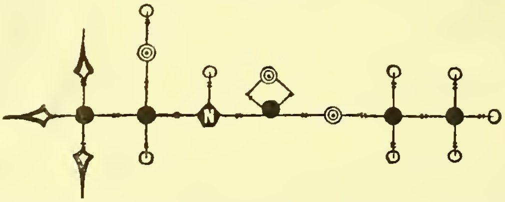
Fig. 1316



Phenyl-urethane, euphorin, $C_9H_{11}NO_2$; m.p. 52°; antiseptic, antithermic, antirheumatic, and analgesic

From urethane some further derivatives are therapeutically employed, *e.g.* a combination of *urethane* and *chloral-hydrate* (fig. 977, p. 272).

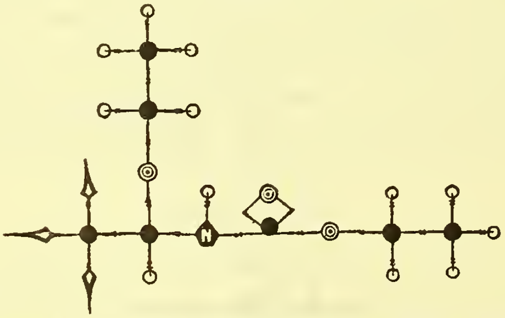
Fig. 1317



Ural, chloral-urethane, $C_5H_8Cl_3NO_3$; m.p. 103°; hypnotic

Ural is supposed to be improved upon by the addition of another ethyl, this time to the *hydroxyl* in chloral:

Fig. 1318

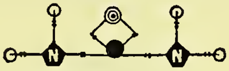


Somnal, $C_7H_{12}Cl_3NO_3$; hypnotic; its existence is not beyond a doubt; some opine that it is merely an alcoholic solution of ural

Neurodine, m.p. 87°, is acetyl-hydroxy-phenyl-urethane, acetyl being joined through an oxygen-atom in para-position to phenyl in fig. 1316, antineuralgic, and thermodine, m.p. 86°–88°, is acetyl-ethoxy-phenyl-urethane, an ethoxy-group being joined in para-position to phenyl and an acetyl-group to the amido-group in phenyl-urethane, fig. 1316; antipyretic.

We next come to those amido-substitution-compounds in which both hydroxyls of carbonic acid have been replaced by ammonia. The first of these is urea, the structure of which we have shown (fig. 1174, p. 328) to be

Fig. 1319



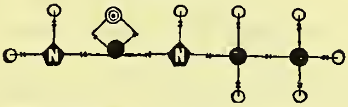
Urea, $CH_4N_2O$

The derivatives of urea may be formed from alkyls and phenyls or from acid radicals; the first are termed alkylated ureas, the last ureïdes.

## Alkylated Ureas

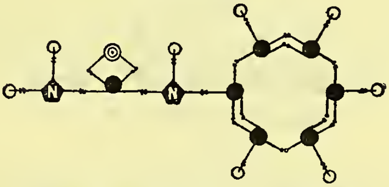
As examples may be mentioned

Fig. 1320



Ethyl-urea, $C_3H_8N_2O$; m.p. 92°

Fig. 1321



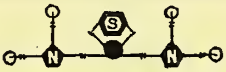
Phenyl-urea, $C_7H_8N_2O$; m.p. 147°

If phenyl urea is ethoxylated we obtain dulcine (fig. 1243, p. 347).

The other hydrogens of urea may also be substituted in a similar way, either symmetrically or asymmetrically. The symmetrical di-phenyl-urea, $C_{13}H_{12}N_2O$, m.p. 235°, is termed carbanilide.

The oxygen in the carbonyl-group may, as we have seen (p. 280), be replaced by *sulphur*:

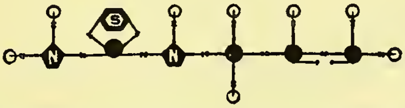
Fig. 1322



Thio-carbamide, thio-urea, sulpho-urea, $CH_4N_2S$; m.p. 171°

A large number of alkylated and acid-derivatives are known, one of them belonging to 'new remedies':

Fig. 1323



Thiosinamine, rhodallin, allyl-thio-carbamide, $C_4H_8N_2S$; m.p. 74°; has been recommended for lupus; its action is said to be confined to the diseased tissue

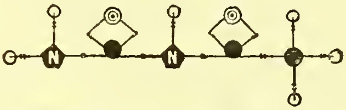
## UREÏDES

These derivatives are combinations of acids with urea. When the acids combine with one molecule of urea they are termed monureïdes, but in the case of di-basic acids they may combine also with two molecules of urea, and are then called diureïdes. The acid combines with its carboxyl-end.

### MONUREÏDES

A combination with *acetic acid* is

Fig. 1324

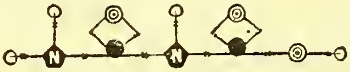


Acetyl-urea, $C_3H_6N_2O_2$; m.p. 212°

Of the combinations of urea with di-basic acids some are of interest.

With *carbonic acid*:

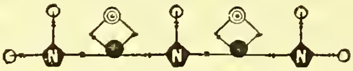
Fig. 1325



Allophanic acid, $C_2H_4N_2O_3$

Allophanic acid cannot exist in the free state, but is split up into urea and carbonic acid. Many salts, however, and ethers are known. An amido-group substituting the hydroxyl ensures its existence. converting it into biuret, the amide of allophanic acid:

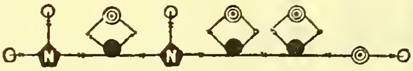
Fig. 1326



Biuret, $C_2H_5N_3O_2$; m.p. 190°

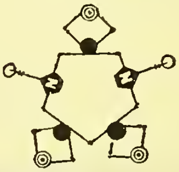
Combination with *oxalic acid* (fig. 712, p. 184) is oxaluric acid, which, on separating a molecule of water, forms a closed chain, parabanic acid.

Fig. 1327



Oxaluric acid, $C_3H_4N_2O_4$; crystalline powder

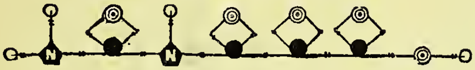
Fig. 1328



Parabanic acid, $C_3H_2N_2O_3$; crystals

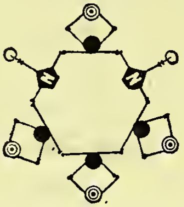
Similarly *mesoxalic acid* (fig. 730, p. 187) forms alloxanic acid and its anhydride, alloxan.

Fig. 1329



Alloxanic acid, mesoxaluric acid, $C_4H_4N_2O_5$ ; crystalline mass. Both carboxyl's and imide's hydrogens are replaceable by metals; the acid is, therefore, considered dibasic

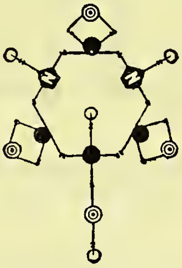
Fig. 1330



Alloxan, mesoxalyl-urea, $C_4H_2N_2O_4$ ; crystals

The cyclo-compound only is known from *tartronic acid* (fig. 726, p. 186), viz. dialuric acid:

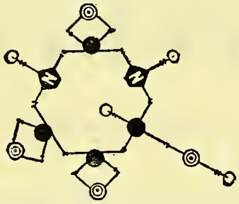
Fig. 1331



Dialuric acid, tartronyl-urea, $C_4H_4N_2O_4$ ; crystals

An isomer is known, the hydroxyl having exchanged places with its neighbouring carbonyl.

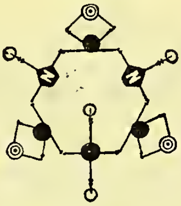
Fig. 1332



Iso-dialuric acid, $C_4H_4N_2O_4$ ; crystals

Also from *malonic acid* (fig. 713, p. 184) the cyclo-compound only is known, viz. barbituric acid.

Fig. 1333

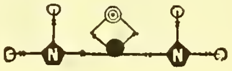


Barbituric acid, malonyl-urea, $C_4H_4N_2O_3$ ; crystals

The two hydrogen-atoms in the methylene-group, $CH_2$, are replaceable by bromine, nitro- and iso-nitroso-groups, metals, and alkyls.

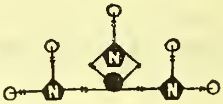
There is a peculiar substitution product of urea with which it runs parallel in many derivatives. It is guanidine, which may be looked upon as urea wherein the oxygen has been substituted by an imido-group.

Fig. 1334



Urea

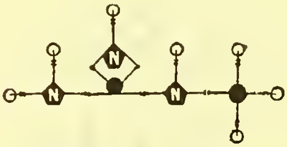
Fig. 1335



Guanidine $CH_5N_3$; crystalline mass

From *guanidine* is derived by introduction of a *methyl-group*:

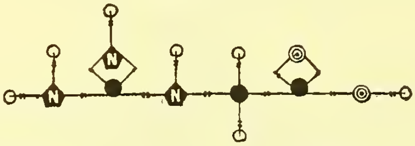
Fig. 1336



Methyl-guanidine, methyl-uramine, $C_2H_7N_3$; deliquescent crystals; the product of bacteria, also of the cholera bacillus; poisonous

When *carbonic acid* is joined to the *methyl-group* of methyl-guanidine it is converted into guanidine acetic acid.

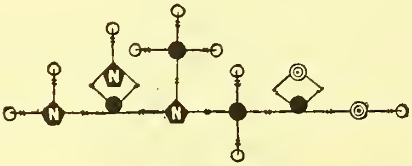
Fig. 1337



Guanidine acetic acid, glycocyamine, $C_3H_7N_3O_2$; crystals

By the introduction of a *methyl-group* creatine is formed:

Fig. 1338

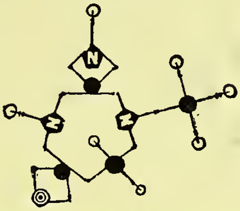


Creatine, methyl guanidine-acetic acid, methyl-glycocyamine, $C_4H_9N_3O_2$; crystals

It is present in the juice of muscle, therefore in beef-extract. By the digestive organs creatine is converted into creatinine, and the greater part of it is found as such in the urine.

Both glycocyamine and creatine assume the cyclo-form by eliminating a molecule of water; creatine is converted into creatinine.

FIG. 1339



Creatinine, glycolyl-methyl-guanidine, methyl-glycocyamidine, $C_4H_7N_3O$; crystals; is always to be found in human urine; an adult man produces daily 0·6–1·3 gramme

Lysatine, $C_6H_{13}N_3O_2$, is a homologue of creatine. It is a decomposition-product of albumin, and urea may be obtained from lysatine.

Lysatinine, $C_6H_{11}N_3O$, is homologous with creatinine, and is also obtained from albuminous substances.

The exact structure of neither is yet known.

## DIUREÏDES[1]

Substances belonging to this class may be looked upon as two molecules of urea united through the chain of an acid; which of the acids serves as the connecting link can be determined from the products formed by splitting them up. Uric acid is the representative of the class, and by the simplest decomposition of the compound it breaks up into *urea* and *alloxan* (fig. 1330, p. 373), which is derived from *mesoxalic acid* and *urea*. Consequently mesoxalic acid (fig. 730, p. 187) must be the connecting link. But it does not perform this duty without undergoing some change; it loses three of its oxygen-atoms, and sufficient hydrogen being at hand it is converted into *acrylic acid* (fig. 738, p. 190). The transformation is represented by the following illustration:

FIG. 1340

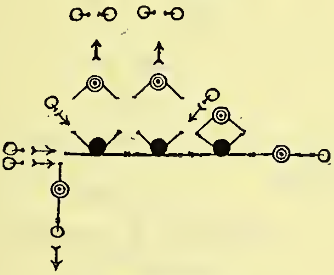


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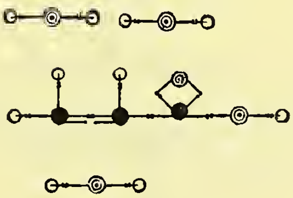
FIG. 1341



Mesoxalic acid = Acrylic acid

Now, instead of constructing our diureïdes from mesoxalic acid, we may be permitted, for the sake of simplicity, to use acrylic acid directly.

---

[1] The class-designation 'diureïdes' is by some chemists reserved for a few compounds consisting of two molecules of a monureïde joining each other; alloxantine, for instance, is two molecules of alloxan joined together, the oxygen of one of the carbonyls (the one at the bottom in fig. 1330, p. 373) being converted into hydroxyl, and the free valency thus created in each alloxane-molecule joining. Purpuric acid is another similar, not isolated, compound, but its structure has not yet been sufficiently ascertained; its ammonium-salt is termed murexide. Our diureïdes are by these chemists classified as 'Xanthine-compounds.'

The first we shall mention is uric acid, composed of two molecules of *urea* and one of *acrylic acid*, eliminating one molecule of water and three of hydrogen:

Fig. 1342

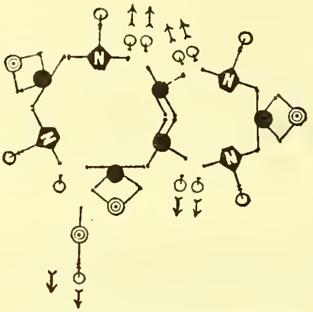
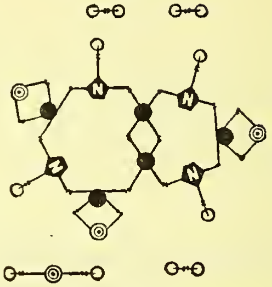


Fig. 1343



Urea + acrylic acid + urea = Uric acid, $C_5H_4N_4O_3$ ; crystals

Uric acid is a normal constituent of human urine. It is soluble in 14,000 parts of water at 20°. Equal parts of lithium carbonate and uric acid dissolve in 90 parts of water at blood-heat; piperazine (fig. 1272, p. 358) is said to dissolve twelve times more uric acid than lithium carbonate; the lithium salt and piperazine are therefore used in diseases arising from over-production of uric acid in the organism; in gout it appears as sodium salt in the blood, being deposited in the joints; urinary concretions usually consist of the ammonium-salt. A healthy man produces daily 0·4—0·8 gramme.

Uric acid is also derived from iso-dialuric acid (fig. 1332, p. 373) and urea, a reaction that gave the clue to the structure

Fig. 1344

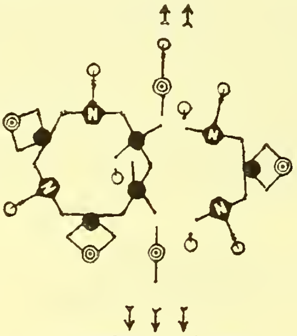
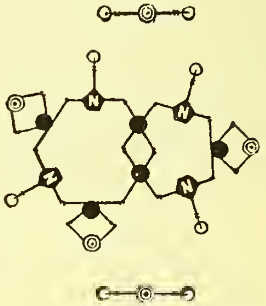


Fig. 1345



Iso-dialuric acid + urea = Uric acid

Another compound, xanthine, is arrived at if acrylic acid in fig. 1342 is turned upside down, eliminating, then, *two* molecules of water and *two* of hydrogen.

Fig. 1346

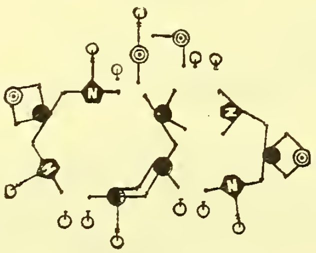
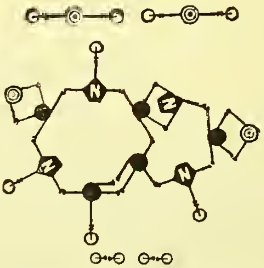


Fig. 1347



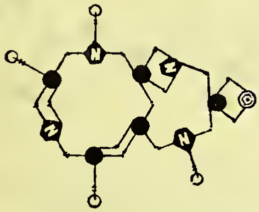
Urea + acrylic acid + urea = Xanthine, $C_5H_4N_4O_2$ ; amorphous powder; occurs in small quantities in different organs of the human body

Hypoxanthine (sarcine), $C_5H_4N_4O$, occurs nearly always together with xanthine, from which it differs by having one oxygen atom less; structure not fully ascertained.

Adenine, $C_5H_5N_5$, has been obtained from the pancreas, from tea-leaves, from decomposition of albuminous substances. It is the imide of hypoxanthine, the relation to which is the same as guanine's to xanthine.

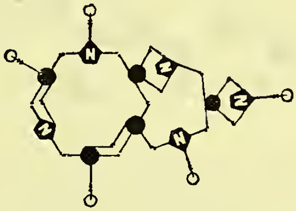
In order to show this relation, I give here an illustration of one of the two possible structures of hypoxanthine and adenine respectively.

Fig. 1348



Hypoxanthine, $C_5H_4N_4O$

Fig. 1349



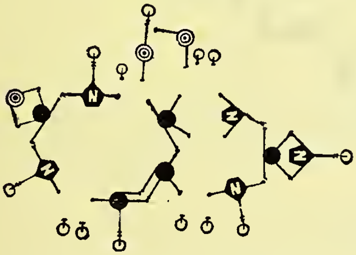
Adenine, $C_5H_5N_5$

It is ascertained that the carbonyl in hypoxanthine has its place in the pentagon (urea); therefore the only other possible structural arrangement is to make the two nitrogen links in the hexagon exchange places (vide *Ber.* xxvi. p. 1914).

It will be seen that the empirical formula of adenine is a polymere of hydrocyanic acid 5(CNH), and in point of fact adenine, when fused with potassium-hydrate, forms potassium-cyanide. In the above structural representation of adenine, four groups placed in positions ready for the formation of hydrocyanic acid are clearly distinguishable.

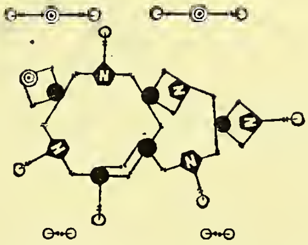
If guanidine (fig. 1335, p. 374) takes the place of one of the ureas in xanthine, **guanine** is formed.

Fig. 1350



Urea + acrylic acid + guanidine =

Fig. 1351

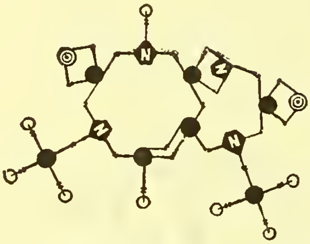


Guanine, $C_5H_5N_5O$; amorphous powder; is present in guano

Some are of the opinion that guanidine replaces the other urea.

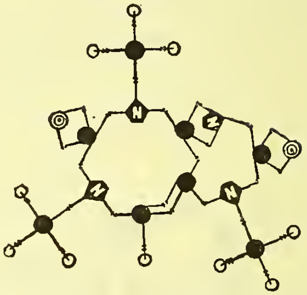
Two or three *methyls* can be introduced into *xanthine*, when we obtain

FIG. 1352



Theobromine, $C_7H_8N_4O_2$ ; crystals, which sublime at 290°; occurs in cocoa-beans; it combines with bases like an acid, but even carbonic acid can separate it from its combinations. The place of methyl in the hexagon is not fully agreed upon; some place it on the other nitrogen in the hexagon

FIG. 1353

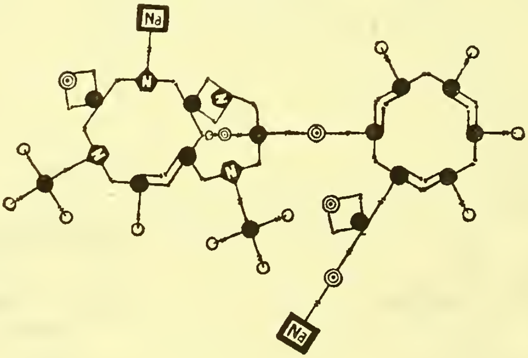


Caffeïne, $C_8H_{10}N_4O_2$ ; m.p. 234° ; occurs in coffee-beans, tea, guarana, Paraguay tea, and in kola-nuts ; in larger doses poisonous

Diuretine is a combination of sodium salicylate and sodium-theobromine, a molecule of each ; but whether it is a chemical compound or a mechanical mixture has not been stated. It is a powerful diuretic without any action on the central nervous system.

If it is a chemical combination its structure would probably be

FIG. 1354

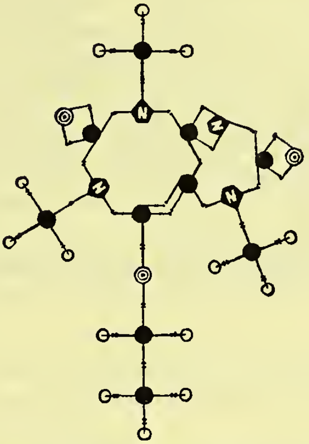


Diuretine, $C_{14}H_{12}N_4O_5Na_2$

Caffeïne is a weak base, and has for medicinal purposes been combined with many acids, such as citric, benzoic, salicylic, cinnamic, carbolic, oxalic, and many other acids ; also an iodine compound has been prepared.

Caffeïne has been improved upon by the introduction of methoxyl or ethoxyl. The latter gives caffeïne this structure:

Fig. 1355



Ethoxy-caffeïne, $C_{10}H_{14}N_4O_3$; m.p. 138°–140°; slightly narcotic with prominent sedative action on the cerebro-spinal system

Methoxy-caffeïne has a similar action.

Nasrol, or *symphorol*, is the sodium salt of sulphonated caffeïne, a new non-poisonous diuretic.

Migrainine is a mixture of caffeïne, antipyrine, and citric acid, recommended for megrim (*Ph. C.* xxxiv. p. 703).

It will be seen how closely allied all the diureïdes are. In fact, xanthine, theobromine, and caffeïne have already been prepared from guanine, or for the matter of that from guano. *Les extrêmes se touchent.*

## Future Nomenclature of Ureas and Guanidines

### Ureas

The name *urea* is to be retained, likewise the division into *ureas* and *ureïdes*; when substitutions take place in both amido-groups, it is proposed to distinguish them as *a* and *b* substitutions. When urea substitutes hydroxyl in *one* of a dibasic acid's carboxyls, the compound is distinguished as *ureïc acid.*

In the case of ureïdes we are left in doubt how to give the proper name to substituents. Ureïdes comprise solely ureas in which *acid*-radicals are substituents; therefore the name may be derived either from the corresponding hydrocarbons, as in acid amides, or from the radical of the acid. If we choose the latter, the division into ureas and ureïdes is superfluous, and if we maintain the class-name ureïdes, the name of the hydrocarbon is quite sufficient. To say *ethane ureïde* would be as correct as *ethanoyl urea*; but to say *ethanoyl ureïde* is to make it, unnecessarily, doubly sure; besides, when the *a* substitute is a hydrocarbon (alcohol-) radical, and the *b* substitute an acid radical, it is difficult to know whether it should be termed an urea or an ureïde. If we describe them all as ureas, and derive the names of acid-derivatives from the acid-radicals, as in the examples below, most difficulties are removed.

| *Old Nomenclature* | | *New Nomenclature* |
|---|---|---|
| Ethyl-urea | (fig. 1320, p. 371) | = No change |
| Di-ethyl-urea | | = *a* : *b* Di-ethyl-urea |
| Ethyl-methyl-urea | | = *a* Ethyl, *b* methyl-urea |
| Acetyl-urea | (fig. 1324, p. 372) | = Ethanoyl-urea |
| Allophanic acid | (fig. 1325, p. 372) | = Methanoyloïc (acid-) urea |
| Biuret | (fig. 1326, p. 372) | = Methanamide-urea |
| Oxaluric acid | (fig. 1327, p. 372) | = Ethanoyloïc (acid-) urea |
| Alloxanic acid | (fig. 1329, p. 373) | = Propanonoyloïc (acid-) urea |
| Thiocarbamide | (fig. 1322, p. 371) | = Thione-urea (?) |

Oxaluric acid is called *l'acide éthanuréidoïque* in *Agenda; Harnstoffäthyloylsäure* is proposed in *Berichte*; and applying the strict Congress rules to the compound, I make it *ethanoyl-ureïc* acid. Still '*il n'y a aucune difficulté dans l'application de ces règles*,' says *Agenda.*

### GUANIDINES

Guanidine itself retains its name, but in all its derivatives it is to be termed *diamino-carbimidine*, with distinguishing indices *a* and *b* for substitutions in the diamino-group, as proposed for urea.

| *Old Nomenclature* | | *New Nomenclature* |
|---|---|---|
| Methyl-guanidine | (fig. 1336, p. 374) | = Methyl-diamino-carbimidine |
| Guanidine-acetic acid | (fig. 1337, p. 374) | = Ethyloïc-diamino-carbimidine |
| Creatine | (fig. 1338, p. 374) | = *a* Methyl-*a* ethyloïc-diamino-carbimidine |

### DIUREÏDES

Diureïdes, as well as many derivatives from one molecule of urea, form closed chains, and their consideration is therefore reserved for a future Congress.

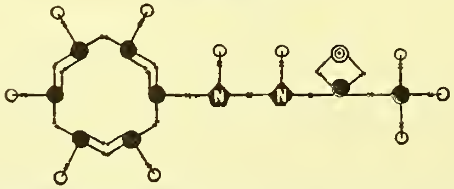
## HYDRAZINE- AND HYDRAZO-DERIVATIVES (p. 332)

(Asymmetrical or *a*- and symmetrical or *β*-hydrazines)

Great efforts have been made to find, from the rather recently discovered phenyl-hydrazine-compounds, some derivatives which might be incorporated into materia medica. The results cannot be said to have been very successful, as with few exceptions all the compounds hitherto tried have proved to be blood-poisons. It has, however, been found that the substitution of radicals for the hydrogens in hydrazine tends to lessen its poisonous character; the more radicals introduced the less poisonous it becomes; but the introduction of more than three radicals has not yet succeeded; perhaps when a way is found to substitute all four hydrogen-atoms something valuable may turn up.

Amongst the compounds which have been therapeutically employed, the following may be mentioned:

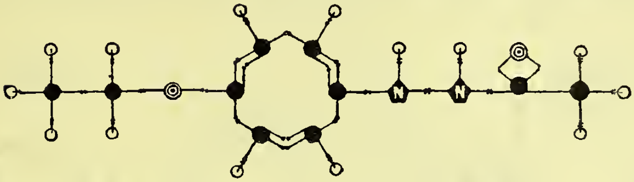
FIG. 1356



Acetyl-phenyl-hydrazine, pyrodine, hydracetine, $C_8H_{10}N_2O$; m.p. 128°·5; used as ointment in psoriasis

Pyrodinum anglicum is a mixture of one part of pyrodine and two parts of some inert powder.

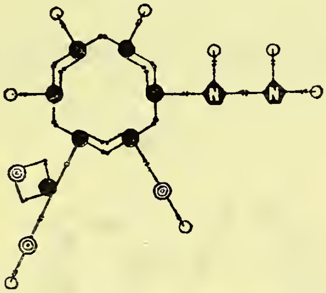
Fig. 1357



*p*-Ethoxy-hydracetine, $C_{10}H_{14}N_2O_2$ (*Ber.* xxv. p. 1848)

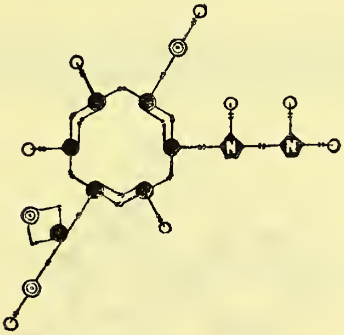
The ethoxyl-group in para-position appears to mitigate the character of similar poisonous compounds (*Ph. Ztg.* 1891, No. 75).

Fig. 1358



Hydrazine-salicylic acid, $C_7H_8N_2O_3$ (*Med. Ann.* 1892, p. 421); used internally and externally for psoriasis

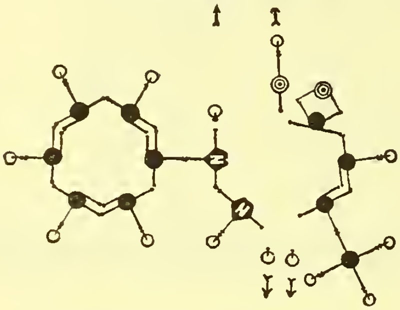
Fig. 1359



Orthine, ortho-hydrazine-para-hydroxy-benzoic acid, $C_7H_8N_2O_3$ (*Ph. C.* xxxi. p. 60); unstable compound; the hydrochlorate has been used as an antipyretic, but is dangerously unreliable; it is a powerful antiseptic (*D. med. Wochensch.* 1890, p. 2)

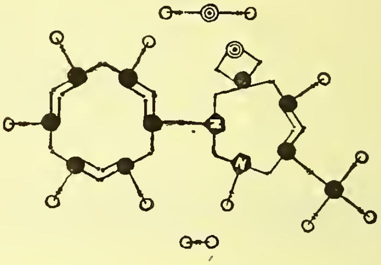
*Phenyl-hydrazine* and *crotonic acid* (fig. 740, p. 190) have structures which apparently would lead to the formation of *antipyrine* by separating a molecule of water and one of hydrogen:

Fig. 1362



=

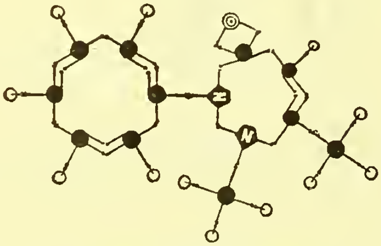
Fig. 1363



Phenyl-hydrazine + crotonic acid = Phenyl-methyl-pyrazolone, $C_{10}H_{10}N_2O$

By adding a methyl-group to the imide-group we should have antipyrine:

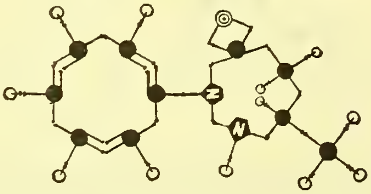
Fig. 1364



Antipyrine (comp. p. 343)

The hydrogen-molecule will, however, not be separated; the atom belonging to phenyl-hydrazine goes over to the crotonic group, breaking its double bond, and instead of phenyl-methyl-pyrazolone a *hydrated* compound is obtained:

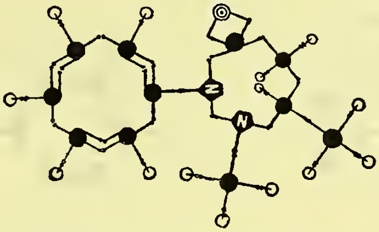
Fig. 1365



Phenyl-methyl-pyrazolidone, $C_{10}H_{12}N_2O$

When methylated, a compound has been obtained which has been called hydro-antipyrine:

Fig. 1366



Hydro-antipyrine, $C_{11}H_{14}N_2O$

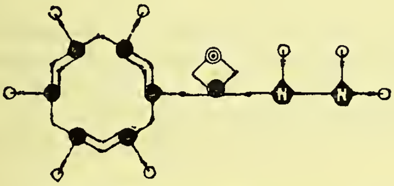
Phenyl-methyl-pyrazolidone can, however, by oxidation, be converted into the mother-substance of antipyrine (*vide* p. 343).

We cannot leave the hydrazines without mentioning an acid, the discovery of which made a great stir in the chemical world a couple of years ago; I refer to azoimide or hydrazoïc acid, which strictly belongs to the inorganic chemistry, as there is no carbon in its structure.

The preparation of hydrazoïc acid was arrived at in the following manner.

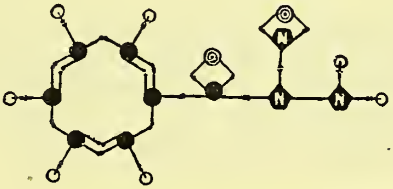
Benzoyl-hydrazine was converted into its nitroso-compound by introducing nitrosyl (fig. 1071, p. 302) into hydrazine.

Fig. 1367



Benzoyl-hydrazine (fig. 792, p. 201)

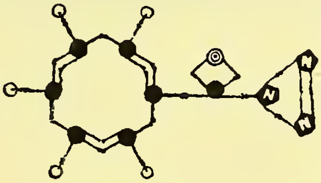
Fig. 1368



Nitroso-benzoyl-hydrazine

Next a molecule of water was withdrawn from the hydrazine group, and four valencies set free, which united thus:

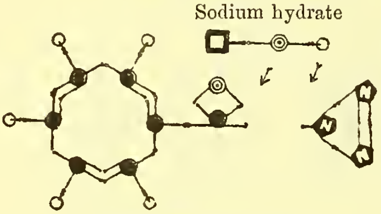
Fig. 1369



Diazo-benzene-imide

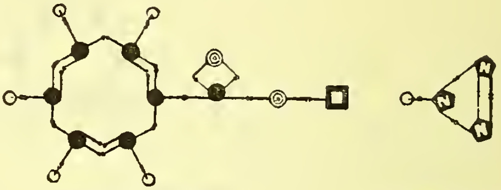
Sodium hydrate will split up this compound into sodium-benzoate and sodium-hydrazoate; by treating the latter with a strong acid the sodium is replaced by hydrogen, and thus the free acid formed. For our illustrative purpose we may condense these two stages of the process into one:

Fig. 1370



Diazo-benzene-imide

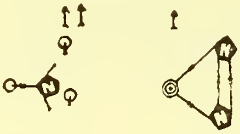
Fig. 1371



Sodium benzoate + hydrazoïc acid, $N_3H$

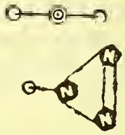
In order to keep my readers up to date, it may be mentioned that the formation of this acid entirely from inorganic bodies has quite recently been successfully performed (*Ber*. xxv. p. 2084). Essentially the preparation is based upon this process:

Fig. 1372



Ammonia + nitrous oxide =

Fig. 1373



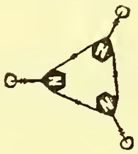
Hydrazoïc acid and water

The two gases, ammonia and nitrous oxide, do not act upon each other, but through the intervention of sodium reaction takes place, of which the above figures represent the extreme phases.

Azoïmide or hydrazoïc acid is a light mobile liquid, b.p. 37°, and a strong acid, *closely resembling hydrochloric acid.* It is, however, very explosive and dangerous to handle.

Judging from the structure of hydrazoïc acid, one would think it possible to add two hydrogens to the molecule, breaking the double bond.

Fig. 1374



This would be the molecule of imide, $N_3H_3$, which is now known only as the radical or group, NH.

# NITROGEN-CYCLO-COMPOUNDS

We have frequently had occasion on the preceding pages to make acquaintance with cyclo-compounds, in which carbon has been replaced by oxygen, sulphur, or nitrogen. I shall only call to mind, amongst *pentagons*, furfurane (fig. 941, p. 260), thiophene (fig. 1015, p. 285) pyrrol (fig. 1182, p. 329); and amongst *hexagons*, pyrone (fig. 945, p. 260), penthiophene (fig. 1017, p. 286), pyridine (fig. 1275, p. 359); and from the *naphthalene* configuration, quinoline (fig. 1304, p. 367). These are but a few examples in which only one carbon-atom is replaced; there are, however, many in which more than one carbon-atom has resigned its position to one or more of the elements mentioned, *e.g.*, thialdine (fig. 1148, p. 322), in which three carbons are replaced, two by sulphur and one by nitrogen. But in point of variety of substitutions, none of the others can compare to the cyclo-compounds in which nitrogen alone is the substituting agent; thus formed, the derivatives of each ring are so numerous that the rings are looked upon as mother substances, and special names have been given to each; if that could have been done methodically and systematically all these names would have tended to facilitate the learning and understanding of chemistry, but their discoveries being unconnected, only spasmodic, and not mutually coherent, attempts have been made; anyhow, we had better have a look at some of them, because there is always the risk of meeting one or other somewhere, although comparatively few are at present of direct interest to medical science.

The mother rings will first be placed side by side, afterwards such derivatives of each as are likely to be of interest will be discussed; with few exceptions the origin of them cannot now be gone into. For some it has already been given (*e.g.* pyrrol, pyridine, quinoline, &c.), for others it is not known, and for the rest they are either merely hypothetical or else wanting sufficient interest.

## Pentagons

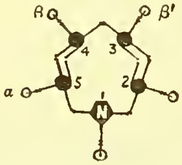
### With one Nitrogen-atom

Azols with seven bonds, two double, three single bonds.

Azolines with six bonds, one double, four single bonds. Azolones if carbonyl present.

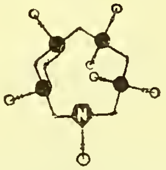
Azolidines with five bonds, no double bond. Azolidones if carbonyl present.

Fig. 1375



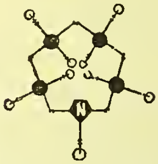
Pyrrol, $C_4H_5N$; b.p. 131°; formation *vide* fig. 1182, p. 329

Fig. 1376



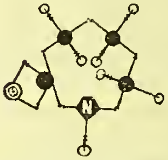
Pyrroline, $C_4H_7N$; b.p. 91°

Fig. 1377



Pyrrolidine, $C_4H_9N$; b.p. 87°

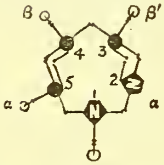
Fig. 1378



Pyrrolidone, $C_4H_7NO$; m.p. 28°

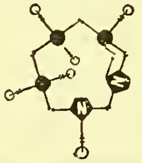
### With two Nitrogen-atoms

Fig. 1379



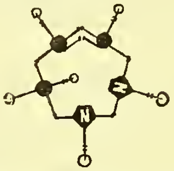
Pyrazol, $C_3H_4N_2$; m.p. 70° (*Ber.* xxiii. p. 1105, xxiv. p. 171)

Fig. 1380



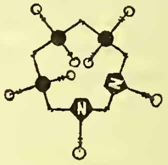
Pyrazoline, $C_3H_6N_2$; a liquid; properties not published (*Ber.* xxvi. p. 408)

Fig. 1381



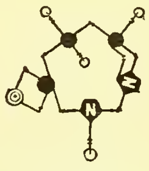
Iso-pyrazoline, $C_3H_6N_2$ (not isolated)

Fig. 1382



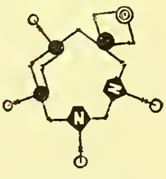
Pyrazolidine, $C_3H_8N_2$ (pyrazine, not to be confounded with pyrazine, fig. 1402, p. 389); not isolated

Fig. 1383



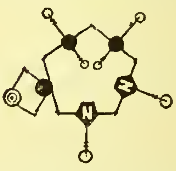
Pyrazolone, $C_3H_4N_2O$; b.p. 152°–157° (*Ber.* xxvi. p. 868)

Fig. 1384



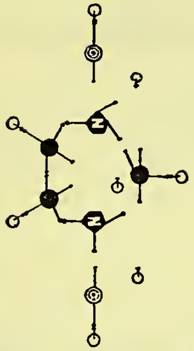
Iso-pyrazolone, $C_3H_4N_2O$; formation, fig. 1234, p. 344

Fig. 1385



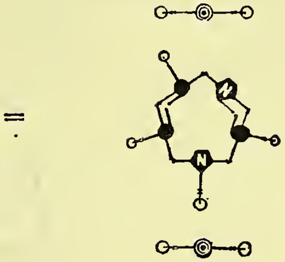
Pyrazolidone, $C_3H_6N_2O$ (*Ber.* xxv. p. 1869)

Fig. 1386



Glyoxime + methane − two molecules of water

Fig. 1387

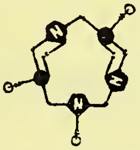


Glyoxaline, $C_3H_4N_2$; m.p. 88°

Theoretically formed from *glyoxime* (fig. 1139, p. 320) and *methane*; actually from *glyoxal* and *ammonia* (see also parabanic acid, creatinine, &c., p. 372, *seq.*)

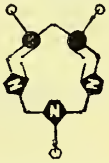
## With three Nitrogen-atoms

Fig. 1388



Triazole, $C_2H_3N_3$; m.p. 120° (*Ber.* xxv. pp. 229, 744)

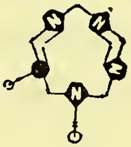
Fig. 1388 a



Osotriazole, $C_2H_3N_3$; m.p. 22°·5; formation from *phenylosazones, osotetrazones*, &c. (*Ann.* cclxii. p. 261)

## With four Nitrogen-atoms

Fig. 1389

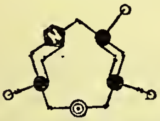


Tetrazole, $CH_2N_4$; m.p. 155°; formation from *amidines* (*Ann.* cclxiii. p. 81, cclxv. p. 129)

## With one Oxygen- and one Nitrogen-atom

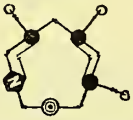
A collective name proposed for these hypothetical compounds is azoxoles.

Fig. 1390



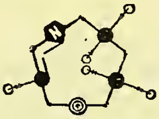
Oxazole, $C_3H_3NO$; formation from *acet-thiamide* and *chloracetone*

Fig. 1391



Iso-oxazole, $C_3H_3NO$

Fig. 1392



Oxazoline, $C_3H_5NO$

### With one Oxygen- and two Nitrogen-atoms (and a Carbonyl)

### (Azoxazoles)

Fig. 1393

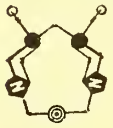


Fig. 1394

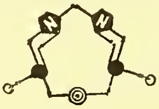
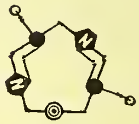
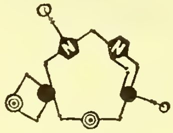


Fig. 1395



Hypothetical furazane, $C_2H_2N_2O$, and isomers; formation from *di-isonitroso-acids* (*Ber.* xxiv. p. 1175, xxv. p. 2163; *Ann.* cclxiv. p. 178)

Fig. 1396



Biazolone, $C_2H_2N_2O_2$; formation from *formyl-phenyl-hydrazine-derivatives* and *phosgen* (*Ber.* xxi. 2456)

# Hexagons

## With one Nitrogen-atom

### (Azines)

Fig. 1397

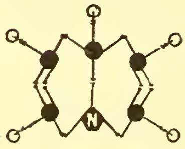


Fig. 1398

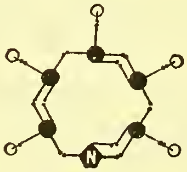
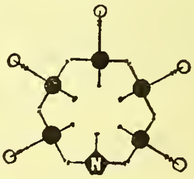


Fig. 1399



Pyridine, $C_5H_5N$; b.p. 116°

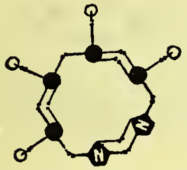
Chemists disagree as to which of these three formulæ is the proper one. Possibly they are all three right, see p. 55, and formation, *vide* fig. 1275, p. 359. The first structure is in point of fact not a hexagon, but two interlocked tetragons, as already frequently mentioned (comp. also acridines, p. 340).

## With two Nitrogen-atoms

### (Diazines)

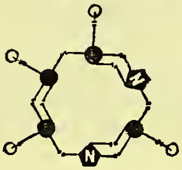
When the two nitrogen-atoms are in ortho-position they are termed oiazines, in meta-position miazines, and in para-position piazines.

Fig. 1400



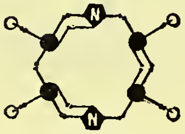
**Oiazine**, $C_4H_4N_2$; hypothetical; only some few rather distant derivatives from this ring are known

Fig. 1401



**Pyrimidine** (*miazine*), $C_4H_4N_2$; hypothetical; formation of oxy-derivatives from *amidines* and *aceto-acetic ether*

Fig. 1402



**Pyrazine** (*piazine*), $C_4H_4N_2$; m.p. 55°; b.p. 115° (*Ber.* xxvi. p. 723); the structure is also represented with a diagonal bond between the two nitrogens analogous to pyridine; formation from *isonitroso ketones*. Derivative: piperazine (fig. 1272, p. 358)

## With three Nitrogen-atoms

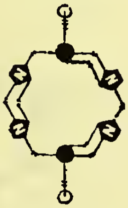
### (Triazines)

*sym*-Triazines, *vide* cyanuric acid and derivatives, p. 423.

## With four Nitrogen-atoms

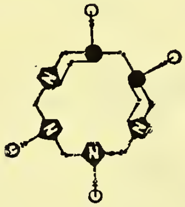
### (Tetrazines)

Fig. 1403



**Tetrazine**, $C_2H_2N_4$; hypothetical

Fig. 1403 A



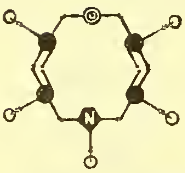
**Oso-tetrazone**, $C_2H_4N_4$; formation from *phenylosazone*

Heptagons, octagons, nonagons, and decagons with nitrogen-atoms are also known.

## Hexagons with one Oxygen- and one Nitrogen-atom

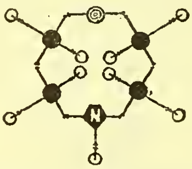
### (Azoxines or Oxazines)

Fig. 1404



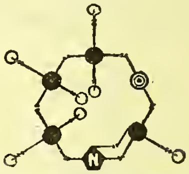
Oxazine, $C_4H_5NO$; hypothetical

Fig. 1404 A



Morpholine, *tetrahydro-oxazine*, $C_4H_9NO$; is said to have been isolated as a piperidine-like base

Fig. 1405

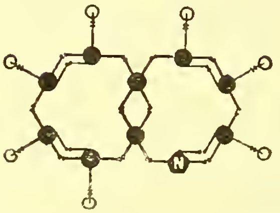


Pentoxazoline, $C_4H_7NO$; formation from *γ-brompropylamine* (*Ber.* xxii. p. 2220, xxiii. p. 2493, xxiv. p. 3213

# Interlocked Rings

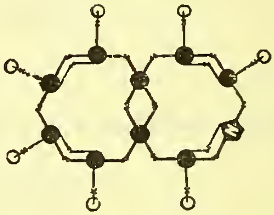
## With one Nitrogen-atom

Fig. 1406



Quinoline, $C_9H_7N$; formation, see fig. 1303, p. 367

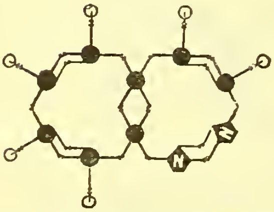
Fig. 1407



Iso-quinoline, $C_9H_7N$; m.p. 23°; b.p. 240°·5

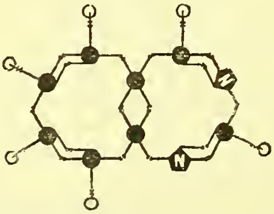
## With two Nitrogen-atoms

Fig. 1408



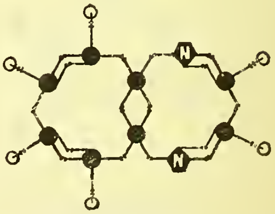
Cinnoline, $C_8H_6N_2$; hypothetical; formation of derivatives from *diazo compounds* (*Ber.* xvi. p. 677)

Fig. 1409



Quinazoline, $C_8H_6N_2$; formation from *ortho-amido-benzamide* and *acid anhydrides* (*Journ. f. pr. Ch.* xxxvi. p. 141)

Fig. 1410



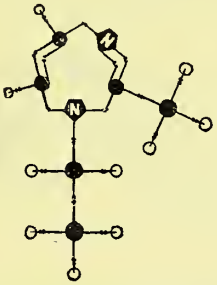
Quinoxaline, quinazine, $C_8H_6N_2$; m.p. 27°; b.p. 229°; formation from *aromatic ortho-diamines* and *glyoxal*, *oxalic acid*, &c. (*Ber.* xvii. p. 319)

## Derivatives from Nitrogen-cyclo-compounds

### Pentagons

We have already had the opportunity of discussing most of those pentagon derivatives which have any claim on our attention, such as *succinimide,* p. 329, *antipyrine,* pp. 343, 344, *ureïdes,* p. 372, *seq.*; further, the many interlocked pentagons; *oxycarbanil,* p. 342, *indole* and *skatole,* p. 352, the derivatives of *amido-acids,* p. 363, and *diureïdes,* p. 375. Besides these, the only one whose derivatives possess interest from a medical point of view is *glyoxaline* (fig. 1387, p. 387), the methyl-ethyl-derivative of which is a base of alkaloïd nature with a narcotic and strongly poisonous character.

Fig. 1411



Ethyl-glyoxal-ethyline, $C_6H_{10}N_2$; b.p. 212°

Ethyl-glyoxal-ethyline acts on the organism like atropine, and paralyses the vagus nerve; but if a hydrogen-atom is replaced by chlorine the new compound, chlor-oxal-ethyline, acts no longer like atropine, but like morphine upon the brain, yet still paralysing the vagus (*Lauder Brunton,* p. 84).

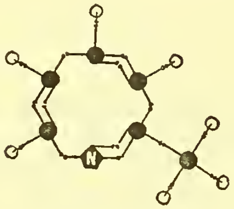
### Hexagons with one Nitrogen (Pyridine-compounds)

Amongst the hexagons pyridine (fig. 1397 &c. p. 388) takes the first place in every respect; nearly all compounds which are now comprised under the designation alkaloïds, and whose structures have been ascertained, have something to do with pyridine.

The derivatives of pyridine are analogous to those of benzene. Pyridine may be hydrated, i.e. the double bonds broken by the introduction of hydrogens inside the ring, or the hydrogens outside, may be replaced in the same way as we have seen those in benzene substituted. The isomers of pyridine-derivatives must, however, be much more numerous than those of benzene's, as the position of the substitutes in regard to nitrogen gives opportunity for many varieties. We shall first look at the substitution products of pyridine.

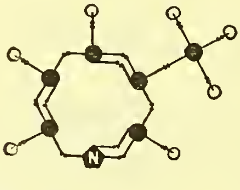
Whereas all carbon-atoms in benzene were of equal value, and consequently only one methyl-derivative, toluene (fig. 232, p. 44), was known, three derivatives from pyridine are not only possible but also known :

Fig. 1412



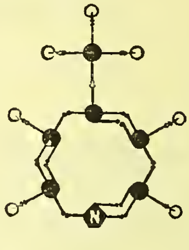
α-Picoline (1 : 2), $C_6H_7N$; b.p. 133°·5

Fig. 1413



β-Picoline (1 : 3), $C_6H_7N$; b.p. 140°-142°

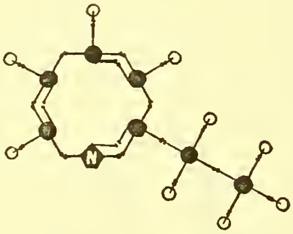
Fig. 1414



γ-Picoline (1 : 4 or *p*-), $C_6H_7N$; b.p. 142°–144°·5

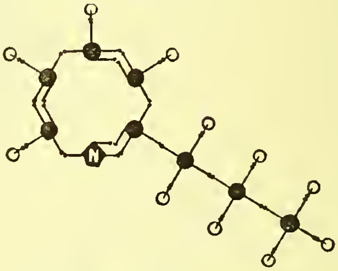
Similarly there are ethyl- and propyl-pyridines &c.:

Fig. 1415



α-Ethyl-pyridine, $C_7H_9N$; b.p. 148°·5 ; three isomers are possible and known

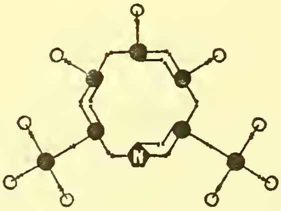
Fig. 1416



α-Propyl-pyridine, conyrine, $C_8H_{11}N$; b.p. 167°; three isomers possible and two known

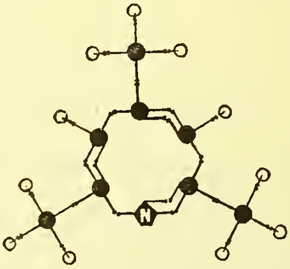
Two or three *methyls* may replace hydrogen-atoms :

Fig. 1417



α-α′-Di-methyl-pyridine, $C_7H_9N$; b.p. 142°

Fig. 1418



*s*-Tri-methyl-pyridine, $C_8H_{11}N$; b.p. 171°

But different alcohol-radicals also may replace hydrogen-atoms in the same molecule ; in this way there are numerous derivatives which have the same empirical formula though they are not identical ; thus we have seen that ethyl-pyridine and di-methyl-pyridine have both the formula

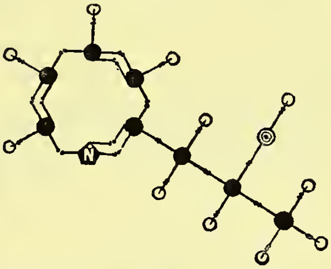
$C_7H_9N$; and *a*-propyl-pyridine and trimethyl-pyridine, $C_8H_{11}N$. All those having the same empirical formula have received their collective names, *e.g.*

| | | | | | |
|---|---|---|---|---|---|
| Pyridine, | $C_5H_5N$ | Collidines, | $C_8H_{11}N$ | Rubidines, | $C_{11}H_{17}N$ |
| Picolines, | $C_6H_7N$ | Parvolines, | $C_9H_{13}N$ | Viridines, | $C_{12}H_{19}N$ |
| Lutidines, | $C_7H_9N$ | Corridines, | $C_{10}H_{15}N$ | Hexyllutidines, | $C_{13}H_{21}N$ |

The theoretical isomers of the last member are almost innumerable, but happily the same law of limitation which we mentioned as existing for the hydrocarbons, p. 18, appears also to obtain here and everywhere. There are nine possible lutidines, of which we know seven; twenty-two collidines are possible (including propyl-, isopropyl-, methyl-ethyl-, and trimethyl-pyridines), of which we know fourteen; there should be hundreds of thousands of hexyllutidines theoretically possible, but all we know is one only.

Alcohols and acids may be formed from pyridine analogous to benzene derivatives. Thus we know, of *alcohols*:

Fig. 1419

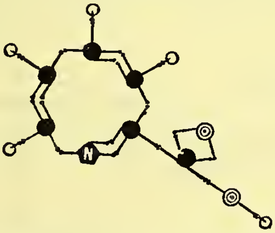


Picolyl-methyl-alkine, $C_6H_{11}NO$

It has both basic and alcoholic properties; such compounds are styled alkines, and their compound ethers (*vide* p. 231) alkeïnes (*Ber.* xiv. p. 1876; comp. p. 321).

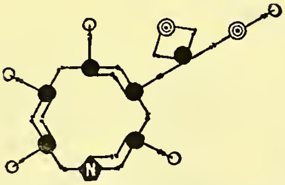
Of *mono-basic acids*:

Fig. 1420



Picolinic acid, *o*- or *α*- or 1 : 2 pyridine-carboxylic acid, $C_6H_5NO_2$; m.p. 135°

Fig. 1421

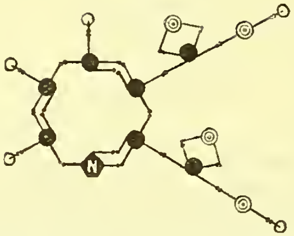


Nicotinic acid, *m*- or *β*- or 1 : 3 pyridine carboxylic acid, $C_6H_5NO_2$; m.p. 228°

The para- or *γ*-acid, iso-nicotinic acid, m.p. 305°, is also known.

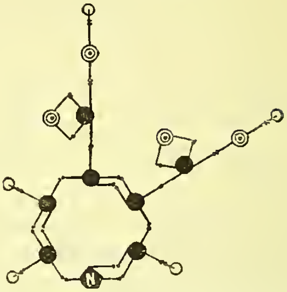
And of *di-basic acids*:

Fig. 1422



Quinolinic acid, *o-m-* or $\alpha\beta$- or 1 : 2 : 3 pyridine-dicarboxylic acid, $C_7H_5NO_4$; m.p. 231°

Fig. 1423

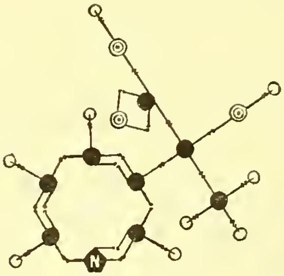


Cinchomeronic acid, *m-p-* or $\beta\gamma$- or 1 : 3 : 4 pyridine-dicarboxylic acid, $C_7H_5NO_4$; m.p. 258°; decomp.

Six of them are theoretically possible and have been prepared.

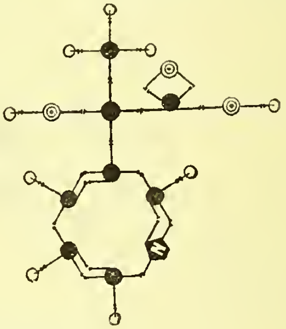
Another mono-basic acid is pyridine's combination with *lactic acid* (fig. 692, p. 179):

Fig. 1424



or

Fig. 1424 a



Pyridine-lactic acid, $C_8H_9NO_3$; a syrupy liquid

From this acid pilocarpidine and pilocarpine may be formed, and *vice versa.* Pyridine-lactic acid has not as yet been prepared in any synthetical, but only derived in the analytical way from pilocarpine; consequently the alkaloïds cannot be said to have been fully prepared by synthesis.

The formation of pilocarpidine is effected by *di-methyl-amine* (fig. 1115, p. 314) replacing the alcoholic hydroxyl; two sets of figures are given below derived from the two structures of pyridine-lactic acid (above), the difference of which is merely in the arrangement of the four links round the central carbon-atom; the first figure in each row is derived from fig. 1424, the others are constructed upon 1424 a in order to show their striking analogy to betaïne, its derivation and derivatives as set out on p. 356.

Fig. 1425

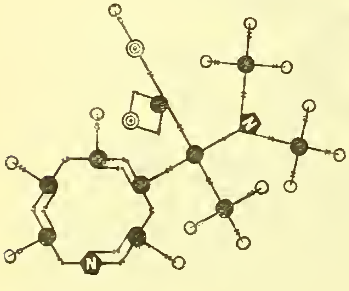


Fig. 1425 a

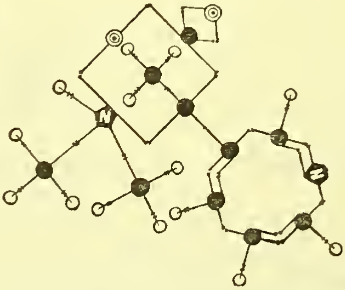
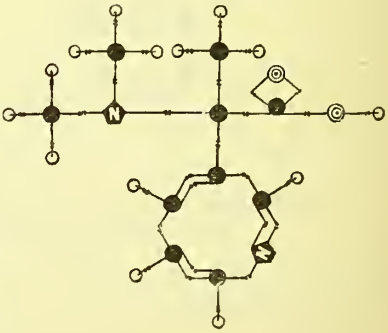


Fig. 1425 b



Pilocarpidine, $C_{10}H_{14}N_2O_2$; deliquescent

Pilocarpidine is one of the three alkaloïds contained in the leaflets of *Pilocarpus pennatifolius* (*Jaborandi,* B.P.), the others being two antagonistic compounds, pilocarpine and jaborine, which sometimes are present in such proportions as to balance each other and render jaborandi inert; an analogous case is that of the poisons in *Agaricus muscarius* (*vide* p. 355). A fourth alkaloïd, jaborandine, closely allied to the others, does not occur in jaborandi, but in the leaves of *Piper reticulatum.*

By transforming the di-methyl-amine group into tri-methyl-ammonium-hydroxide (comp. fig. 1124, p. 316) we obtain

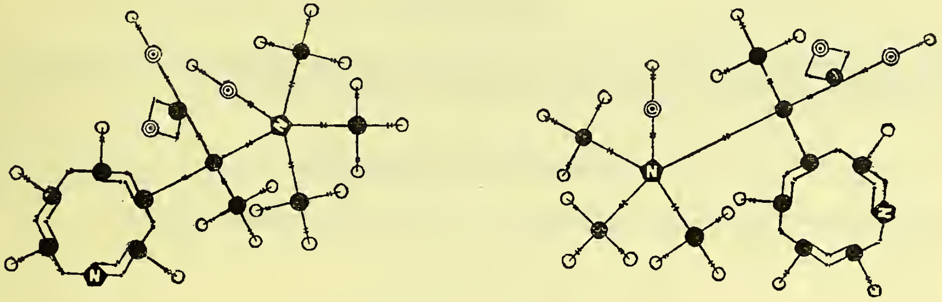


Fig. 1426

Fig. 1426 a

Pilocarpic acid, $C_{11}H_{18}N_2O_3$

The proximity of the alcoholic and carboxylic hydroxyls (proper regard being had to the stereometrical form of fig. 1426a) makes it possible to withdraw a molecule of water, and the two free valencies will join:

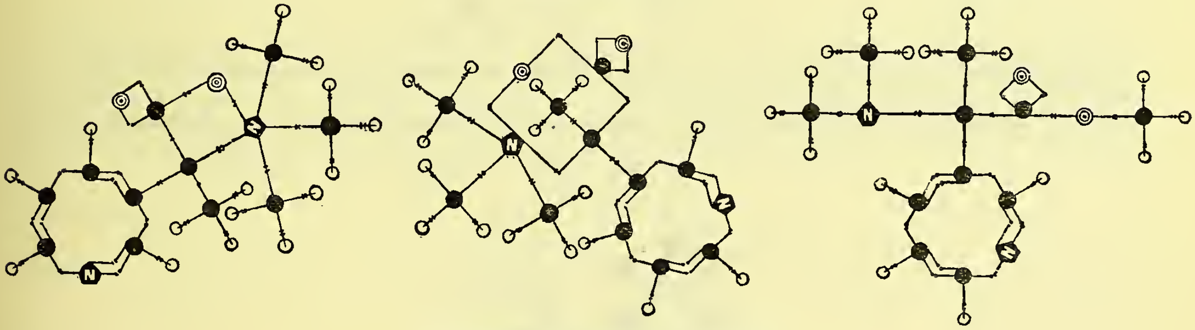


Fig. 1427

Fig. 1427 a

Fig. 1427 b

Pilocarpine, $C_{11}H_{16}N_2O_2$; amorphous

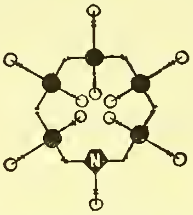
The structures of jaborine and jaborandine have not yet been fully ascertained.

## Hydrated Pyridines

Four or six hydrogen-atoms may be introduced into the pyridine-ring, breaking a corresponding number of double bonds. By the introduction of six atoms, piperidine (fig. 1274, p. 359) is formed; we have before (*l.c.*) derived it from penta-methylene-diamine.

The structure of piperidine was this:

Fig. 1428



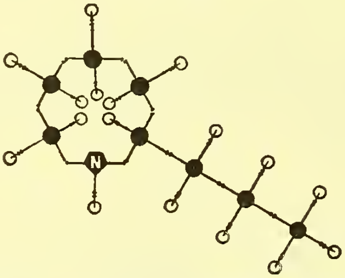
Piperidine, $C_5H_{11}N$

We can by substitution affix side-chains to this ring, such as alcohol- and acid-radicals, or replace the hydrogen-atom in the imido-group by nitrosyl (fig. 1067, p. 301) &c.

## Piperidine-derivatives

If *propyl* replaces the hydrogen in *a*-position, we obtain the alkaloïd conine:

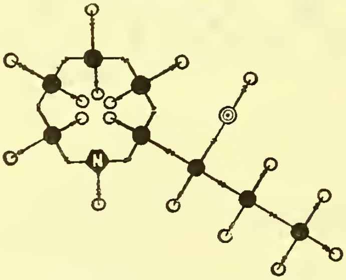
Fig. 1429



Conine, *a*-normal-propyl-piperidine, $C_8H_{17}N$; b.p. 167°; the poisonous principle of *Conium maculatum* (hemlock)

If a hydroxyl is introduced into the side-chain another alkaloïd, conhydrine, is formed:

Fig. 1430



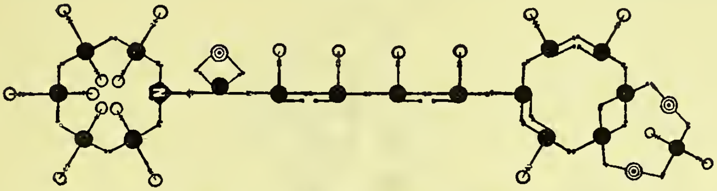
Conhydrine, conydrine, *a*-piperidyl-ethyl-alkine, $C_8H_{17}NO$; m.p. 121°. (Mark the similarity in the name conyrine, fig. 1416, p. 392)

The position of the hydroxyl is not conclusively ascertained; it may be on the carbon-atom at the end of the side-chain, in which case conhydrine would be lupetidylalkine (comp. p. 397). As regards the distinction of this alkaloïd as an alkine, *vide* footnote, p. 321.

It is found together with conine in hemlock.

Amongst the acids with which piperidine may combine is *piperic acid* (fig. 833, p. 221):

Fig. 1431

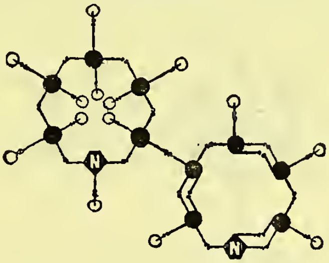


Piperine, $C_{17}H_{19}NO_3$; m.p. 129°; is found in different species of *Piper nigrum* and *longum*

The homologues of piperidine (i.e. hydrated picolines, lutidines, and collidines, *vide* p. 393) have been distinguished as pipecolines, $C_5H_{10}N\ (CH_3)$, lupetidines, $C_5H_9N\ (CH_3)_2$, copellidines, $C_5H_8N\ (CH_3)_3$.

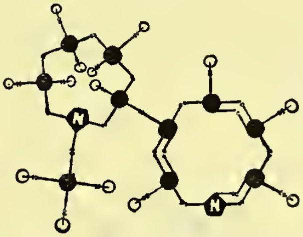
Finally piperidine was supposed to combine with pyridine and to form a structure, which was, until quite recently, accepted as that of nicotine:

Fig. 1432



The above structure represents two pyridine-rings, of which one is hydrated (piperidine), the other not. Recent investigations (*Ber.* xxvi. p. 292) have, however, made the existence of a piperidine-ring doubtful; according to them it is much more probable that the nitrogen in the supposed piperidine-ring is connected with a methyl. In that case the ring would be a methylated pyrrolidine (fig. 1377, p. 386), and the structure of nicotine would be

Fig. 1433



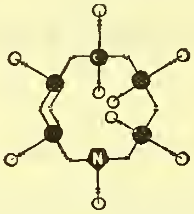
Nicotine, $C_{10}H_{14}N_2$; oily liquid; b.p. 247° (257 mm.)

Other structures with triangular or quadrangular rings, instead of a pentagon, have still more recently been submitted (*Ber.* xxvi. p. 628); the question of the structure is, thus, far from settled.

Nicotine, to the extent of from 0·6 to 8 per cent., occurs in combination with malic and citric acid in tobacco; smoking destroys the greater part of it, but some of the nicotine escapes with the smoke, which latter contains also a variety of decomposition products, partly pyridine or derivatives; that from pipes contains mainly pyridine, that from cigars collidines (p. 393).

When four hydrogen-atoms are added to pyridine we obtain a compound which has received the name of piperideïne or tetrahydro-pyridine:

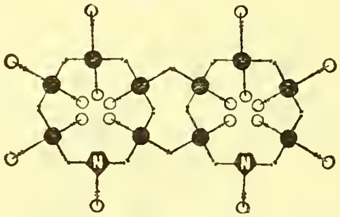
Fig. 1434



Piperideïne, $C_5H_9N$

it does not, however, appear to exist at ordinary temperatures, two molecules joining into a double molecule.

Fig. 1435



Di-piperideïne, $C_{10}H_{18}N_2$; m.p. 61°

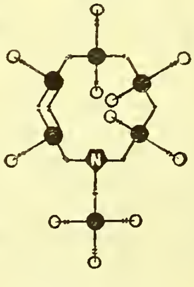
When heated it dissociates (p. 278), and each double molecule is divided into two molecules, piperideïne.

## Derivatives of Piperideïne

however exist and count among them some of our most important alkaloïds.

The greater part of them are derivable from a hypothetical methyl-piperideïne, in which methyl has replaced the imido-hydrogen:

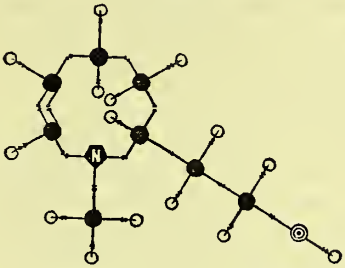
Fig. 1436



Methyl-piperideïne

A hydroxy-ethyl introduced in *a*- (*o*-) position converts this into hydroxy-ethyl-methyl-piperideïne, or

FIG. 1437

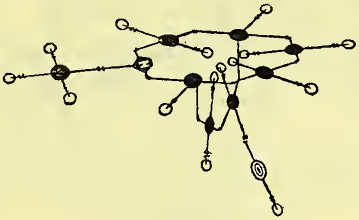


Tropine, $C_8H_{15}NO$; m.p. 62°

Tropine is strictly a cyclo-hydramine (p. 321), but being a tertiary base has been distinguished as an alkine.

Another (perspective) structure for tropine has been propounded (*Ber.* xxiv. p. 3108), analogous to the one given for tri-ethylene-diamine (fig. 1273, p. 359):

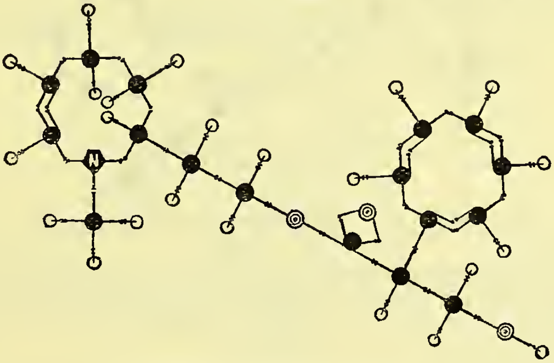
FIG. 1438



This makes it a combination of hydrated *phenol* and *methyl-piperideïne* if we look upon the right horizontal half-hexagon as belonging to both the left half and to the flap hanging down; anyhow, for practical considerations, we will make use of the first structure.

Tropine combines, ether-fashion, with *tropic acid* (fig. 819, p. 214), and forms atropine.

FIG. 1439



Atropine, $C_{17}H_{23}NO_3$; m.p. 113°

Atropine exists in three optical isomers.

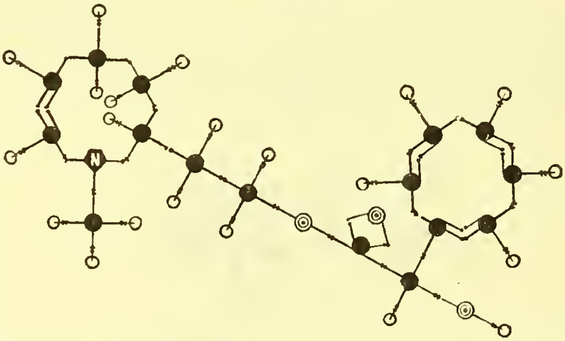
Atropine is an antidote to muscarine, and because the symptoms of poisoning with the latter show a close resemblance to those of the cholera (*Lauder Brunton*, p. 63), atropine has been suggested as a remedy in cholera cases. The idea has been put to the test, and with great success so far (meeting of the Royal Medical and Chirurgical Society, June 1893).

Daturine is identical with atropine, and occurs in *Atropa belladonna* and *Datura strammonium*.

Hyoscyamine and hyoscine (*hyoscyn*) are isomers with atropine (*Ber.* xxv. p. 2388). Scopolamine has the empirical formula $C_{17}H_{21}NO_4$ (*Arch. d. Ph.* 1892, p. 207), but the structure is not known of any of them. Commercial hyoscine seems to be sometimes mixed with scopolamine, at other times entirely scopolamine. Duboisine is probably a mixture of hyoscyamine and hyoscine. By treating hyoscyamine with alkali it is converted into atropine.

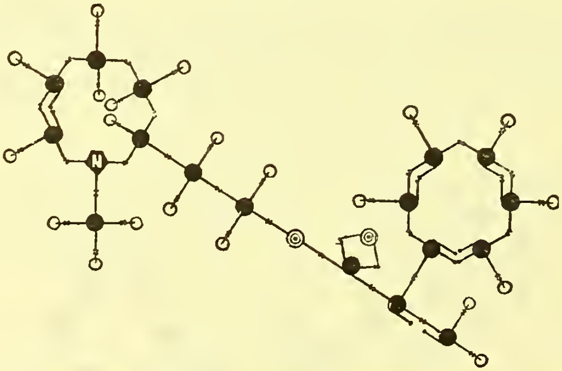
Other acids than tropic acid have been united to tropine: amongst them are *sulphuric*, and of course *salicylic acid*, but more especially *mandelic acid* (fig. 816, p. 213) and *atropic acid* (fig. 820, p. 214), both nearly related to tropic acid, and one of which has been successful in forming a valuable remedy. The first forms homatropine, the other apoatropine[1]:

Fig. 1440



Homatropine, $C_{16}H_{21}NO_3$; m.p. 95°–98°; less poisonous than atropine, but its mydriatic effect less lasting

Fig. 1441



Apoatropine, $C_{17}H_{21}NO_2$; m.p. 60°; has no mydriatic action; produces in larger doses characteristic convulsions

Atropamine is believed to be identical with apoatropine (*Ph. C.* xxxiii. p. 353; *Merck's Ber.* 1893). It is derivable from atropine by the separation of a molecule of water. By dilute hydrochloric acid it is converted into belladonine, another alkaloïd, probably an isomer, found together with atropine in *Atropa belladonna* &c.

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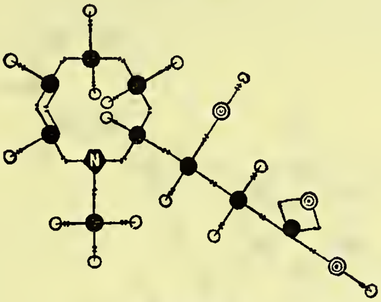
[1] The prefix *hom-* or *homo-* is an abbreviation for 'homologous,' i.e. the compound is a derivative differing by $CH_2$ from the mother substance; *apo-* simply means 'derived from,' but how, we know not, or at least we did not at the time of its discovery.

Tropine was formed, as we have seen, from methyl-piperideïne and hydroxy-ethane (or its radical hydroxy-ethyl); if, instead of the latter, we take hydroxy-propionic acid (hydracrylic acid, fig. 693, p. 179), the first step is made towards forming another very important alkaloïd, cocaïne. The structure of this combination of methyl-piperideïne and the acid, ecgonine, is

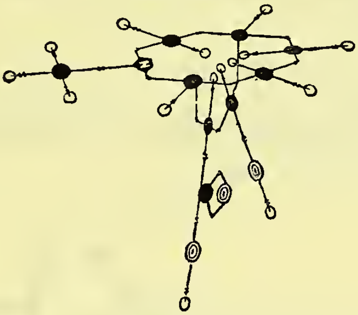
Fig. 1442



Ecgonine, $C_9H_{15}NO_3$; m.p. 198°; dextro- and lævo-rotatory ecgonines are known

In analogy to tropine (fig. 1438, p. 399) a combination structure has been suggested (*Ber.* xxiv. p. 3108)

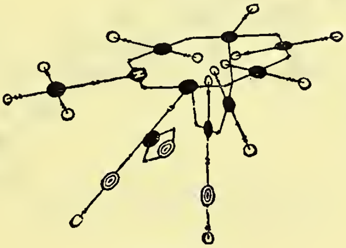
Fig. 1443



Ecgonine

in which later researches (*Ber.* xxvi. p. 325) have made the carboxyl exchange places with the hydrogen of the group CH next to the nitrogen-group:

Fig. 1443 a



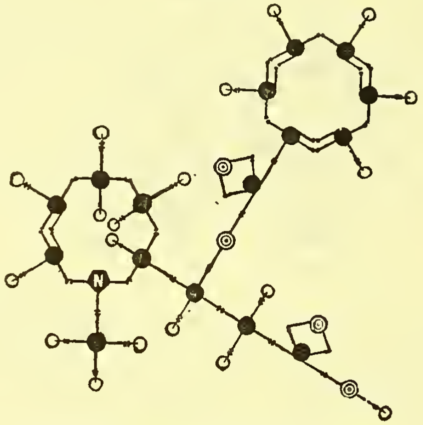
Ecgonine

From ecgonine cocaïne has been synthetically built up, but ecgonine itself has not as yet been so prepared. The only way to get it has been to pull cocaïne or some allied alkaloïds to pieces;

like the synthesis of pilocarpine, that of cocaïne can be said to have been but half performed; but no doubt it will be carried out some day.

The alcoholic hydroxyl can be joined in ether-fashion to benzoic acid, the result being

Fig. 1444

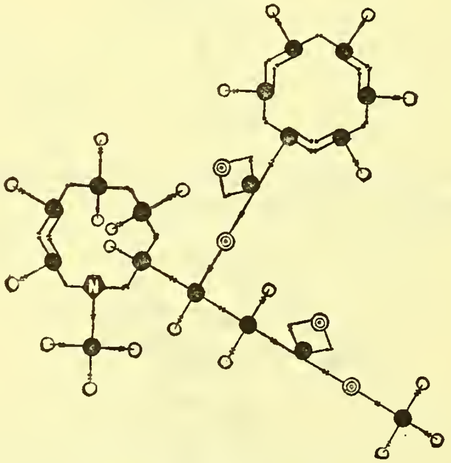


Benzoyl-ecgonine, $C_{16}H_{19}NO_4$; m.p. 90°

Benzoyl-ecgonine occurs in the coca leaves. Its action is somewhat similar to that of caffeïne, but not to that of cocaïne.

All we now have to do to make cocaïne is to place a methyl at the end of the carboxyl, another etherification:

Fig. 1445



Cocaïne, $C_{17}H_{21}NO_4$; m.p. 98°

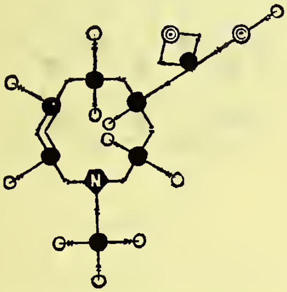
There are a dextro- and a lævo-rotatory cocaïne; it is the latter that occurs in the coca leaf. Dextro-cocaïne has m.p. 43°, and is an artificial product, stereo-isomeric to, and formed from, cocaïne, and has similar properties.

Cocethyline, or *homo-cocaïne,* is formed by introducing ethyl instead of methyl in the last-mentioned operation.

Cinnamyl-cocaïne results when cinnamic acid (fig. 821, p. 214) is used for etherification instead of benzoic acid.

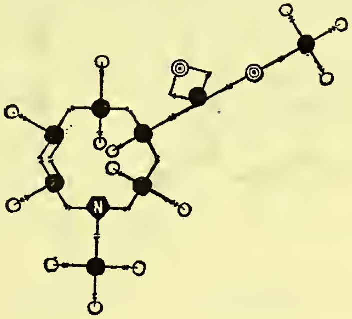
In the *areca-nut* two alkaloïds are present, derivable from methylated and tetrahydrated pyridine or methyl-piperideïne ; there are also an acid, arecaïdine, and its methyl-ether, arecoline, both related to, and also synthetically prepared from, nicotinic acid (fig. 1421, p. 393). *Vide Ph. C.* xxxiii. p. 13 ; *Arch. Ph.* 1891, ix. p. 669.

Fig. 1446



Arecaïdine, $C_7H_{11}NO_2$ ; is therapeutically inactive

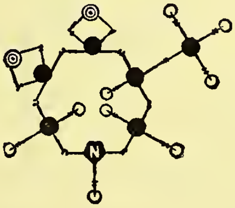
Fig. 1447



Arecoline, $C_8H_{13}NO_2$ ; oily liquid ; is the only anthelmintic principle in the areca-nut ; poisonous like pilocarpine and partly like pelletierine ($C_8H_{15}NO$), an alkaloïd of unknown structure from *Punica granatum*

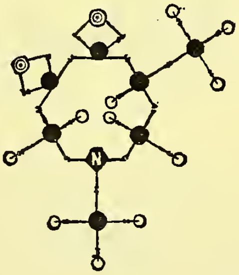
The two alkaloïds found in the areca-nut are inert, and contain two carbonyl-groups ; their relation to the others will easily be understood from the illustrations :

Fig. 1448



Guavacine, $C_6H_9NO_2$

Fig. 1449

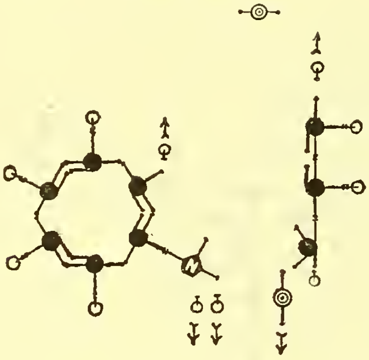


Arecaïne, $C_7H_{11}NO_2$

## Quinoline-derivatives

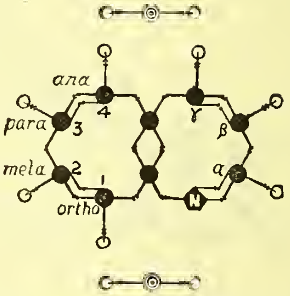
When a pyridine-ring is interlocked with a benzene-ring we call the compound quinoline. We have already mentioned its formation from *o*-amido-cinnamic aldehyde (fig. 1303, p. 367); another formation is from *aniline* (fig. 1111, p. 313), and *acroleïn* (fig. 548, p. 133):

Fig. 1450



Aniline + acroleïn

Fig. 1451



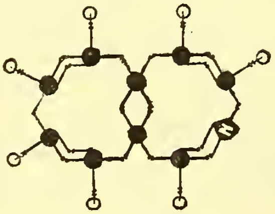
Quinoline, $C_9H_7N$; b.p. 236°

Acroleïn may be prepared from glycerin (p. 133); therefore quinoline is by this reaction prepared from aniline and glycerin, being heated together with sulphuric acid, which takes away the water, and nitrobenzene, which provides the necessary oxygen to form the water, as shown above.

This synthesis caused some sensation at the time, and has been named, after its discoverer, *Skraup's synthesis.*

In coal-tar, where quinoline is found ready formed, another compound also occurs that differs from quinoline in the position of the nitrogen which has been found placed in *α*-position:

Fig. 1452

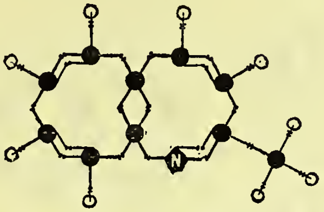


Iso-quinoline, $C_9H_7N$; m.p. 22°; b.p. 240°

It has also been synthetically prepared, and is important as mother substance of several alkaloïds.

If, in the formation of quinoline, we take *alkylated acroleïns*, i.e. the higher homologues, instead of acroleïn, we obtain alkyl substituted quinolines, with the substitute in the pyridine-ring (N.B.: the homologues join with their ends reversed and the bonds re-arranged); *e.g.* croton-aldehyde (fig. 549, p. 133) forms α-methyl quinoline:

Fig. 1453

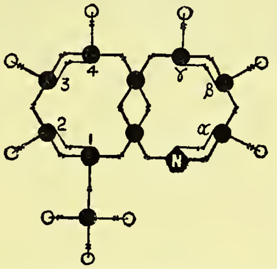


Quinaldine, α-methyl-quinoline, $C_{10}H_9N$; b.p. 138°

It is also designated as *py*-α-methyl quinoline, *py*- indicating substitution in pyridine-ring.

If aniline is alkylated, e.g. *o*-toluidine (fig. 1112, p. 313), we obtain a quinoline with substitution in the benzene-ring, toluquinoline:

Fig. 1454



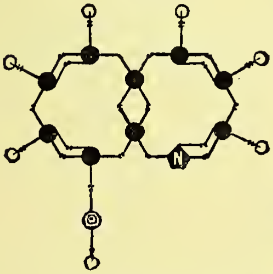
*o*-Toluquinoline, *bz*-1-methyl-quinoline, $C_{10}H_9N$; b.p. 248°

*bz*- indicates that the substitution has taken place in the benzene-ring; the numeral signifies the position. This designation by *bz*- and *py*- seems rather superfluous when the position in the benzene-ring is indicated by numerals, and in the pyridine-ring by Greek letters.

A great number of isomers of these alkylated quinolines are both possible and known.

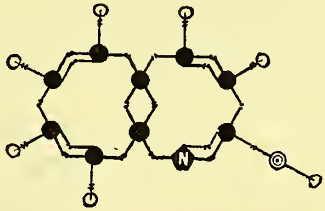
When hydroxyl replaces a hydrogen-atom in quinoline it is termed an oxyquinoline (hydroxyquinoline), if the substitution takes place in the benzene-ring; but a carbostyril if the hydroxyl is placed in the pyridine-ring.

Fig. 1455



Quinophenol, *o*-*bz*-1-oxyquinoline, $C_9H_7NO$; m.p. 75°;

Fig. 1456



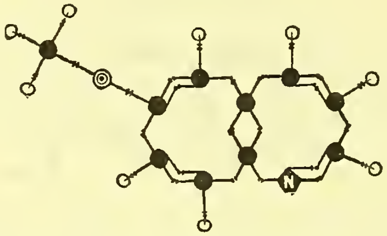
Carbostyril, *py*-2- (or α-) oxyquinoline, $C_9H_7NO$; m.p. 200°

Six out of seven possible isomers have been prepared

The formation of carbostyril and its tautomeric form, pseudo-carbostyril, from amido-cinnamic acid has already been discussed, p. 366.

Through their hydroxyls these oxy-quinolines may form ethers, *e.g.*

Fig. 1457



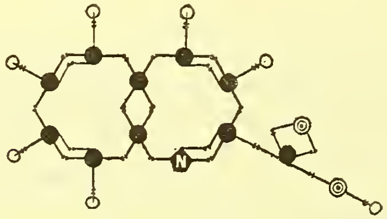
Quinolidine, quinanisol, *p*-methoxy-quinoline, $C_{10}H_9NO$ ; b.p. 304° (740 mm.)

It may be synthetically prepared according to Skraup's method from p-*amido-anisol* (anisol, *vide* fig. 494, p. 116) and *acroleïn* (comp. p. 404).

Carboxyls may also be fixed upon quinoline and the derivatives mentioned, in different positions converting them into acids.

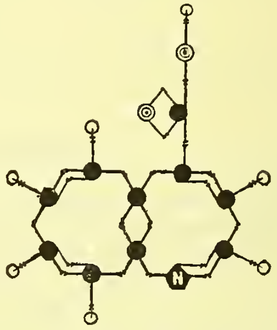
Thus we have from *quinoline* itself

Fig. 1458



Quinaldinic acid, α-quinoline-carboxylic acid, $C_{10}H_7NO_2$ m.p. 156°

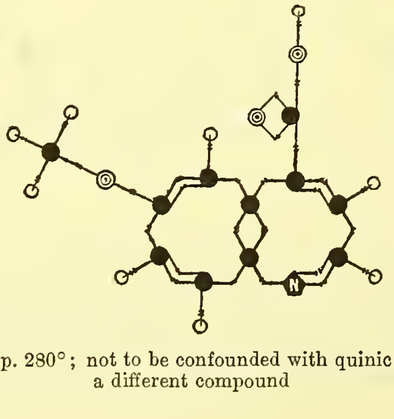
Fig. 1459



Cinchoninic acid, γ-quinoline-carboxylic acid $C_{10}H_7NO_2$ ; m.p. 253°

and from *quinolidine*

Fig. 1460



Quininic acid, $C_{11}H_9NO_3$ ; m.p. 280° ; not to be confounded with quinic acid (fig. 809, p. 210)—quite a different compound

Of a more complex structure are the following 'new remedies':

Fig. 1461

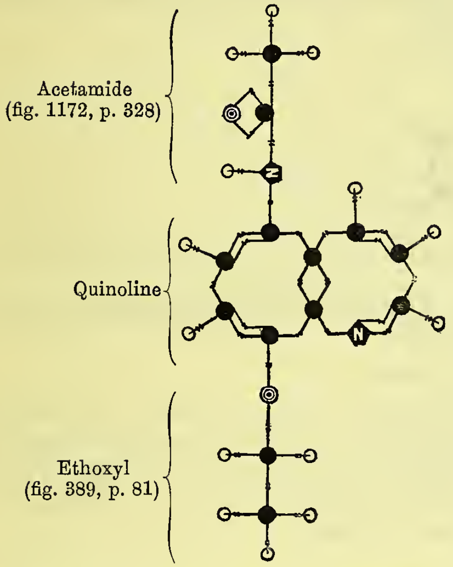
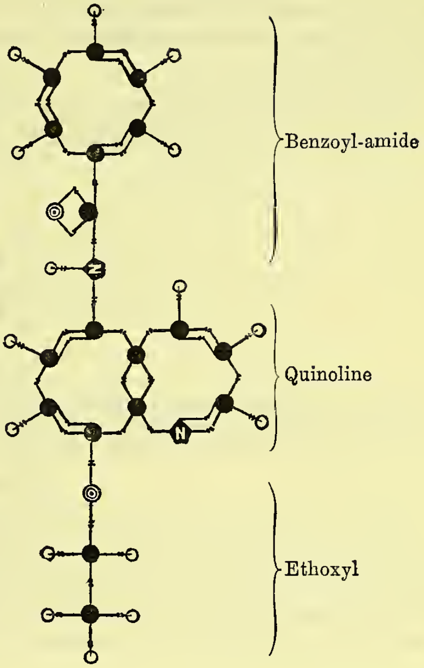


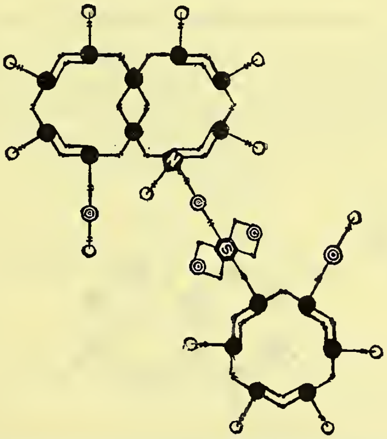
Fig. 1462



Analgene, *ortho*-oxethyl (ethoxyl)-*ana*-monacetyl-(or benzoyl)-amido-quinoline, $C_{13}H_{14}N_2O_2$; m.p. 155° (*Ph. C.* xxxii. p. 433); antipyretic and antirheumatic. Observe the analogy to phenacetine, saliphene, &c., pp. 348 *seq.*

Analgene was originally started as an acetyl compound (the first figure), but has recently appeared as a benzoyl-compound (the second figure) (*Benz-analgene, Ph. C.* xxxiii. p. 727).

Fig. 1463



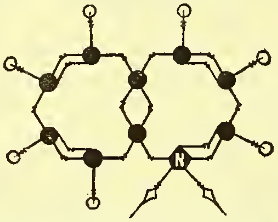
Diaphterine, oxyquin-aseptol, ortho-phenol-oxy-quinoline-sulphonate, $C_{15}H_{13}SNO_5$; non-poisonous, antiseptic

Diaphterine is a combination of hydroxy-quinoline (fig. 1455, p. 405) and aseptol (fig. 1045, p. 292), nitrogen appearing in the character of a pentad (*Ph. C.* xxxiii. p. 320; *Ph. Ztg.* 1892, p. 317).

Later researches have established the presence of two molecules of hydroxy-quinoline in the compound, the second substituting the hydrogen in aseptol's hydroxyl, exactly in the same manner as the first has substituted hydrogen in the sulphonic acid; accordingly its chemical formula would be $C_{24}H_{20}SN_2O_6$.

Iodine and chlorine are said (*Heger's Synopsis*) to enter into the quinoline-structure as additions to the nitrogen by its changing from a triad into a pentad:

Fig. 1464



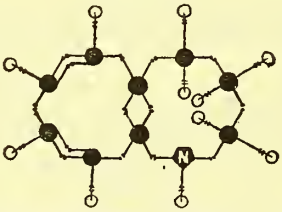
Quinoiodine, $C_9H_7NICl$; antiseptic and antithermic; used in *phthisis* and *angina pectoris*

It is, perhaps, more probable that the halogens substitute the hydrogens in α- and β-positions, analogous to di-chloro-quinoline (*Beilst*, iii. p. 746); the empirical formula would then be $C_9H_5NICl$.

## Hydrated Quinolines

Like all closed chains built on the benzene pattern, hydrogens may be added to the rings of quinoline by breaking the double bonds. Thus di-, tetra-, hexa-, and deka-hydro-quinolines have been formed, the pyridine-ring being by preference first filled, and only when that cannot accept any more (four) hydrogen-atoms, the benzene-ring is entered. Of these, tetra-hydro-quinoline is important on account of its relation to some well-known alkaloïds:

Fig. 1465

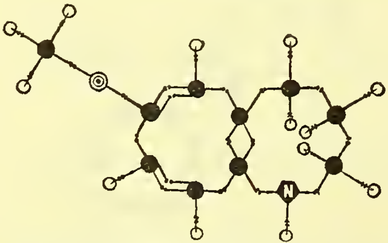


Tetra-hydro-quinoline, $C_9H_{11}N$; b.p. 244°

It is an interesting compound in so far as it formed the starting-point for the preparation of several alkaloïd-like substitutes for *quinine*. These derivatives have mostly been superseded by other and better compounds, but as they have historical interest they are worth mentioning.

Thus by introducing a methoxyl in the para-position thalline was obtained:

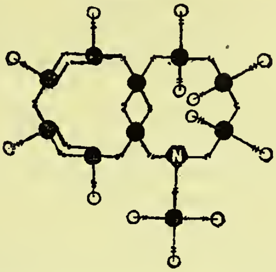
Fig. 1466



Thalline, para-methoxy-tetrahydro-quinoline, $C_{10}H_{13}NO$; m.p. 42°; is still used for fevers in children, and in typhoid as a sulphate, tartrate, or hydrochlorate

With a *methyl* fixed to the *nitrogen* kaïroline is obtained

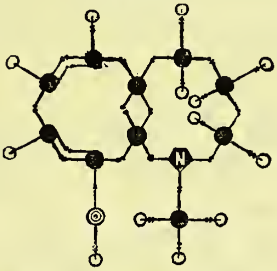
Fig. 1467



Kaïroline, methyl-tetrahydro-quinoline, $C_{10}H_{13}N$; b.p. 242°

A hydroxyl may be introduced in ortho-position, producing

Fig. 1468



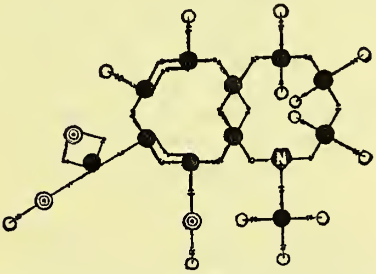
*o*-Hydroxy-methyl-tetrahydro-quinoline, $C_{10}H_{13}NO$; m.p. 114°; febrifuge

The *chloride* is termed kaïrine, or kaïrine *M.*

If ethyl is joined to nitrogen instead of methyl it is distinguished as kaïrine *A.*

When a *carboxyl* replaces the meta-hydrogen in *methyl-kaïrine,* we get another new antipyretic:

Fig. 1469



Hydroxy-methyl-tetrahydro-quinoline-carboxylic acid, $C_{11}H_{13}NO_3$; antipyretic

The sodium salt has been awarded the trade name thermifugine.

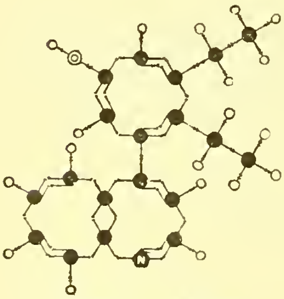
We now come to the alkaloïds contained in the barks of the various species of *cinchona*, and derivable from a combination of tetra-hydro-quinoline with quinoline, as far as their structures have as yet been ascertained.

The cinchona bark contains a great variety of things: six acids (amongst them quinic acid and oxalic acid have been determined), three neutral substances, and twenty-four bases at least.

The structures of two of the bases, viz. cinchonine and quinine, have probably, up to a certain point, been ascertained.

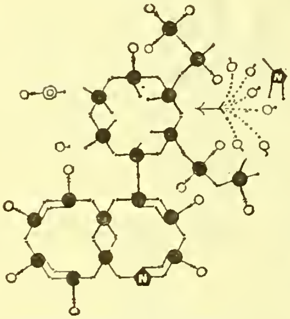
Cinchonine, the empirical formula of which is $C_{19}H_{22}N_2O$, can, by removal of a molecule of water, be converted into a compound termed cinchene, $C_{19}H_{20}N_2$. From this compound a molecule of ammonia, $NH_3$, can be split off, but at the same time a molecule of water re-enters the compound, which then is termed apocinchene, $C_{19}H_{19}NO$. The structure of apocinchene has been ascertained in its main features (*Ber.* xxvi. p. 713); it consists of a combination of *quinoline* and a *di-ethylated phenol*, in which the positions of hydroxyl and the two ethyls have not yet been ascertained with exactitude; so much is, however, known, that their *relative* positions are either 1 : 2 : 3 or 1 : 3 : 4. Provided, therefore, that we have apocinchene we should be able to prepare cinchonine by reversing the above processes, viz. first by introducing ammonia and splitting off water, forming cinchene, and secondly by introducing again water, forming cinchonine. We can illustrate these processes in the following way, giving to hydroxyl and the two ethyls in apocinchene the relative positions 1 : 3 : 4, merely because the different groups come out better thus in the illustrations:

Fig. 1470



Apocinchene, $C_{19}H_{19}NO$;
m.p. 209°–210°

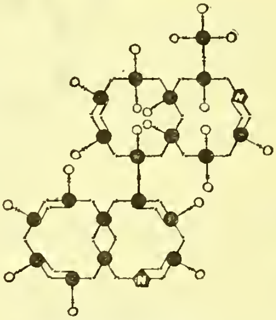
Fig. 1470 A



Apocinchene + ammonia
− water

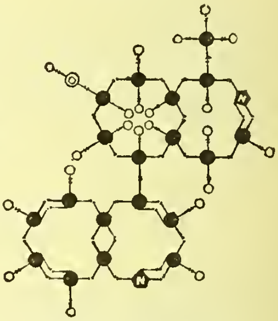
=

Fig. 1470 B



Cinchene, $C_{19}H_{20}N_2$;
m.p. 123°–125°

Fig. 1471



Cinchonine, $C_{19}H_{22}N_2O$;
m.p. 268°·8 (cinchene + water)

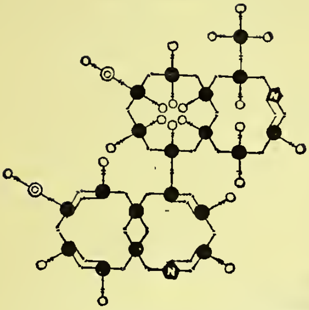
Cinchonine would, according to this structure, be quinoline combined with a hydroxylated, methylated, and hydrated iso-quinoline.

Cinchonine is known for certain to be a di-tertiary base with a hydroxyl outside a quinoline group; still the above representation is not quite the correct structure of cinchonine, because it has been ascertained (*Monatsh.* xii. and xiii.) that two molecules of hydroiodic acid can be *added* to the structure besides one that converts the compound into the hydroiodic salt. None of these enter into the quinoline group, though the evidence, upon which this assertion rests, does not seem quite conclusive, and in the iso-quinoline group, as represented above, there is room for only two molecules of hydroiodic acid, one breaking the double bond and the other forming the salt by turning the nitrogen into a pentad. The illustrations are therefore only intended to give an idea of our present knowledge of the subject.

Cupreïne. In the bark of *Cinchona cuprea* or of *Remijia pedunculata* an alkaloïd is present, which has been called cupreïne: it is nearly related to cinchonine, the difference between them being a hydroxyl, which is affixed to the quinoline-ring in cupreïne.

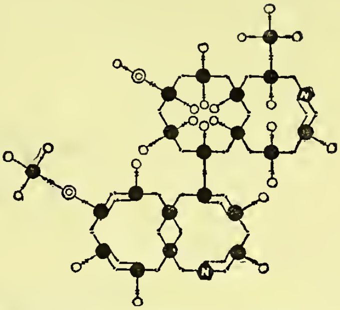
Quinine differs from cupreïne by the presence of a methyl-group joined to the aforesaid quinoline-hydroxyl. For the sake of illustration we will suppose the above structure of cinchonine (fig. 1471) to be correct; cupreïne's and quinine's structures may then be illustrated thus:

FIG. 1472 A



Cupreïne, $C_{19}H_{22}N_2O_2$ ; m.p. 198°

FIG. 1472 B



Quinine, $C_{20}H_{24}N_2O_2$ ; m.p. 177°

As will be seen, quinine is the methyl-ether of cupreïne.

The synthesis of quinine and the allied alkaloïds has not yet succeeded; the synthetical preparation of apocinchene through phenyl-quinoline is being investigated, and will probably be carried out before long, and quinine has already been prepared from cupreïne by substituting methyl for hydrogen in the hydroxyl of the quinoline group (*Compt. Rend.* cxii. p. 774); but how apocinchene is to be converted into cupreïne or cinchene is not yet discovered.

Quinidine and cinchonidine are isomers (possibly stereometrical) of quinine and cinchonine respectively.

Homoquinine, also a base found in the bark of *Cinchona cuprea,* is a combination of one molecule of quinine and one molecule of cupreïne.

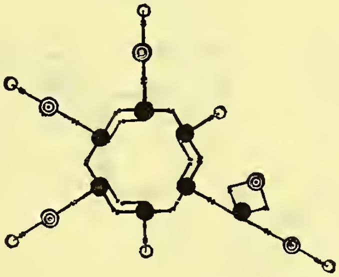
Antiseptol is the *sulphate* of one of the above-mentioned *iodine-compounds* of cinchonine. It is employed in lieu of iodoform.

We are next coming to a couple of alkaloïds of special interest, because we have succeeded in pulling them to pieces, and by so doing have been enabled to see how the building should be put together, though we have not profited so much by it that we can perform the same work as our Grand Master.

The two are: narcotine, one of the opium-alkaloïds, and hydrastine, found in the root of *Hydrastis canadensis.* They have a further interest to us in the analogy of their formation. Though we do not know actually how to build them up from the foundation-stone, methane, it is easy enough to do so on paper; and because, as a rule, it is more pleasant to build up than to pull down, we will do so here, and commence with narcotine.

From methane is derived, through several intermediary stages which have already, but disconnectedly, been described (more fully illustrated under the next alkaloïd, p. 414), an acid which we know by the name of *gallic acid* (fig. 834, p. 221):

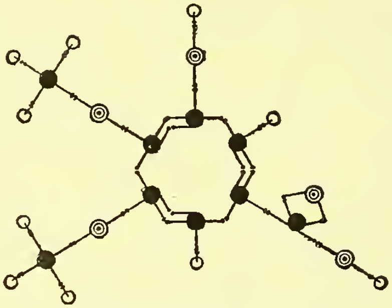
FIG. 1473



Gallic acid, $C_7H_6O_5$

We combine by etherification two methyls with this acid:

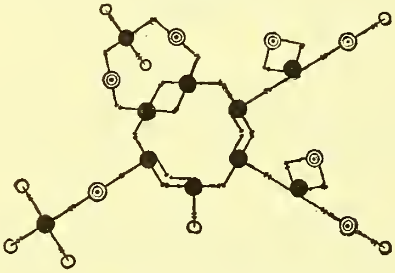
Fig. 1474



Di-methyl-gallic acid, $C_9H_{10}O_5$

By oxidation we can split off two hydrogen-atoms, one from hydroxyl and the neighbouring methyl respectively, and at the same time introduce another carboxyl:

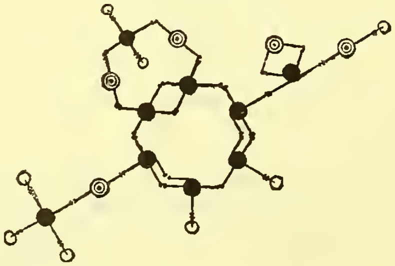
Fig. 1475



Cotarnic acid, $C_{10}H_8O_7$

For similar formation see safrol, fig. 504, p. 120.
The first carboxyl may then be split off:

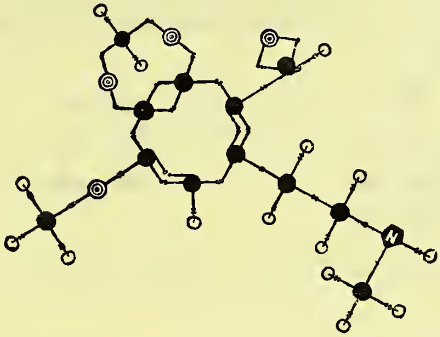
Fig. 1476



Methyl-methylene-gallic (pyro-gallol-carbonic) acid, $C_9H_8O_5$; m.p. 210°

This acid may be reduced to aldehyde and simultaneously combined with methyl-ethyl-amine.

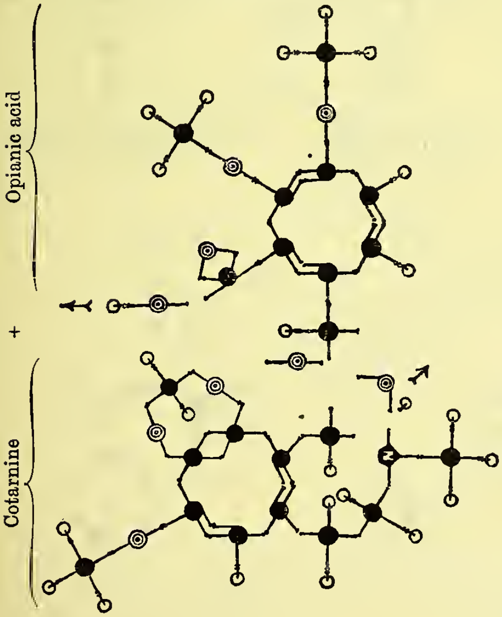
Fig. 1477



Cotarnine, $C_{12}H_{15}NO_4$ ; m.p. 132°

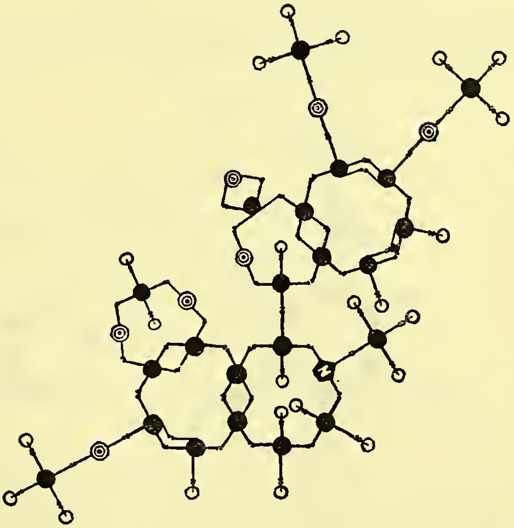
If cotarnine is brought together with opianic acid (fig. 922, p. 253) they join, through their aldehydes which are present in the structure of both, but not before these aldehydes have each formed an interlocked ring with its nearest side-chain, cotarnine forming an *iso-quinoline ring* (fig. 1452, p. 404), and opianic acid, *meconine* (fig. 924, p. 254).

Fig. 1478



=

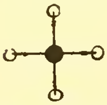
Fig. 1479



Narcotine, $C_{22}H_{23}NO_7$ ; m.p. 176°

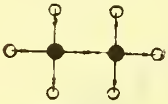
Hydrastine has been investigated in the same way, and very interesting analogies have turned up. They have been arrived at by pulling down, as was the case with narcotine, but we will again choose the reverse method, and commence with the very source of all organic bodies, methane, as it may perhaps prove interesting to see the gradual growth from this our simplest hydrocarbon to one of the more complex compounds, just as we have with narcotine, but not so fully. It will now be sufficient to give the figures and refer to their respective places in this treatise.

Fig. 1480



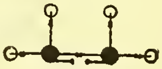
Methane (fig. 14, p. 7)

Fig. 1481



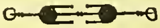
Ethane (fig. 41, p. 12)

Fig. 1482



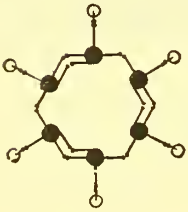
Ethylene (fig. 179, p. 35)

Fig. 1483



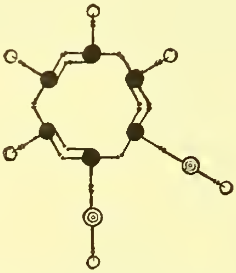
Acetylene (fig. 206, p. 39)

Fig. 1484



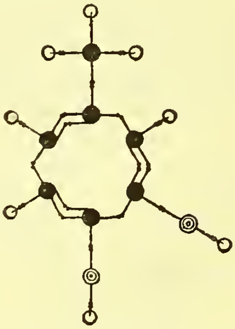
Benzene (fig. 157, p. 32)

Fig. 1485



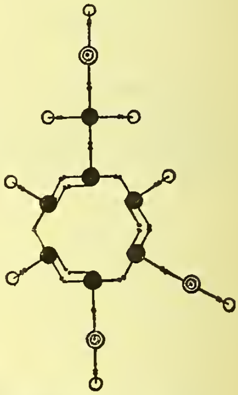
Pyrocatechin (fig. 418, p. 92)

Fig. 1486



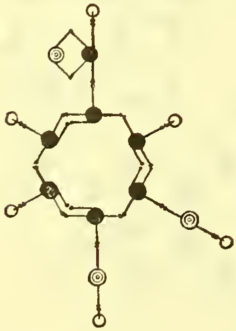
Homo-pyrocatechin (fig. 431, p. 96)

Fig. 1487



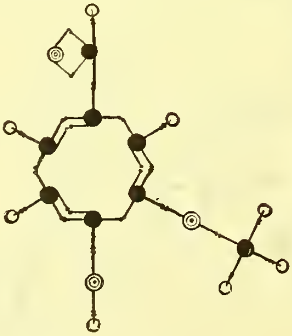
Protocatechuic alcohol (fig. 463, p. 106)

Fig. 1488



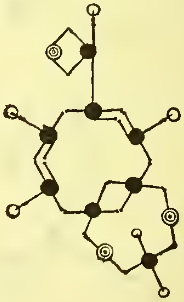
Protocatechuic aldehyde (fig. 561, p. 136)

Fig. 1489



Vanillin (fig. 562, p. 136)

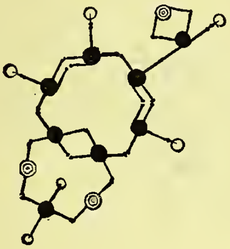
Fig. 1490



Piperonal (fig. 564, p. 137)

Compare now piperonal with methyl-methylene-gallic acid (fig. 1476, p. 412), because the analogies between narcotine and hydrastine are becoming more striking. For comparison's sake we lay piperonal a little over on the side:

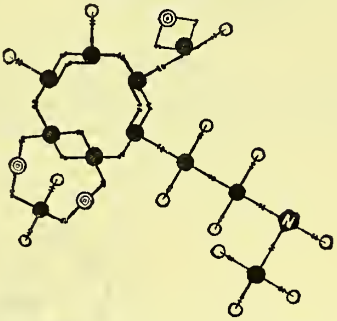
Fig. 1491



Piperonal

and combine it with methyl-ethylamine:

Fig. 1492



Hydrastinine, $C_{11}H_{13}NO_3$; m.p. 116°

When hydrastinine is brought together with *opianic acid*, hydrastine is formed by a process entirely analogous to the formation of narcotine from cotarnine and opianic acid:

Fig. 1493

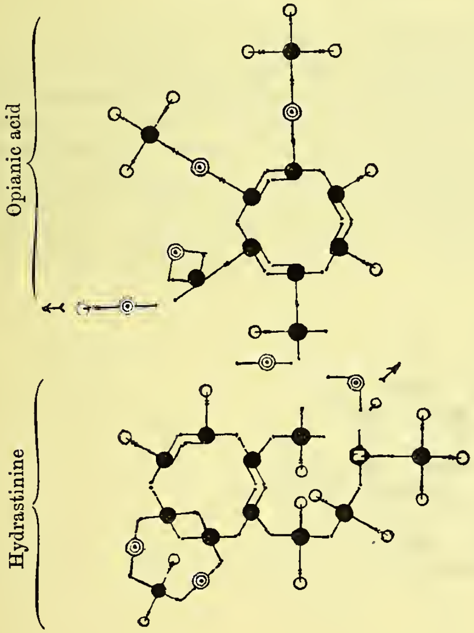
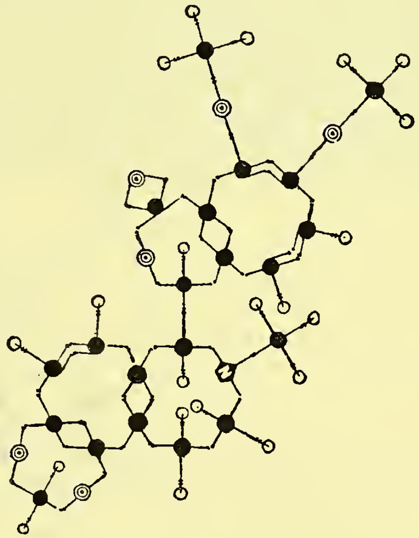


Fig. 1494



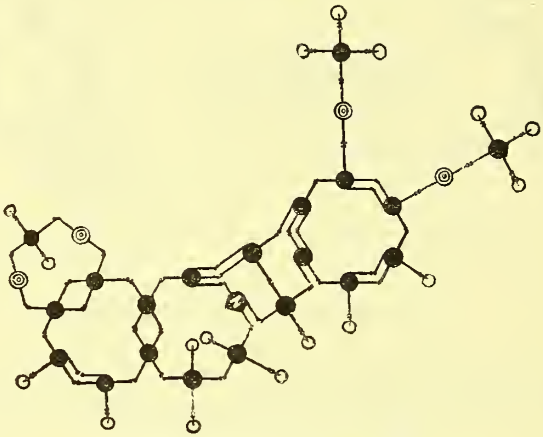
Hydrastine, $C_{21}H_{21}NO_6$; m.p. 135° (*Ann.* cclxxi. p. 311)

As pointed out before, this building up of hydrastine is merely theoretical; the reverse way, commencing with hydrastine and finishing with methane, is, however, actual.

An *alcoholic extract* of the root of *Hydrastis canadensis*, prepared in America, is also called hydrastine.

Another alkaloïd presenting several points of analogy to the two preceding ones is **berberine**, found together with two more alkaloïds (*oxyacanthine* and *berbamine*) in the root of *Berberis vulgaris.* I shall only give the structure of it (*Journ. Ch. Soc.* 1889, p. 63; 1890, p. 992), and leave to the reader to find out for himself the similarities, and to build it up from methane; it is as good as any average Christmas puzzle:

Fig. 1495

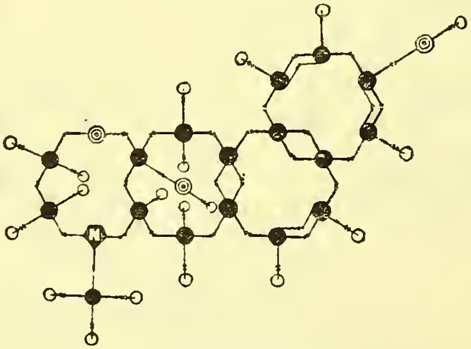


Berberine, $C_{20}H_{17}NO_4$; m.p. 120°

Attention is invited to the anthracene-like connection between the two chief-groups.

Besides those already discussed (meconine and narcotine) there are some twenty other constituents of opium. Of these there are three acids—*meconinic acid* (fig. 923, p. 254), *lactic acid* (fig. 692, p. 179), and *sulphuric acid*—the rest are bases. Some of the latter are more or less related to narcotine, most of them are found in such small quantities that the researches on their structure have been considered less important. The most important of all, **morphine**, has, however, been the subject of much investigation, but its nature does not seem to have been entirely disclosed. It used to be considered a pyridine-derivative, but more recent investigations point to a phenantrene- (fig. 151, p. 31) compound, of which the following structure has been suggested (*Ber.* xxii. p. 1113):

Fig. 1496

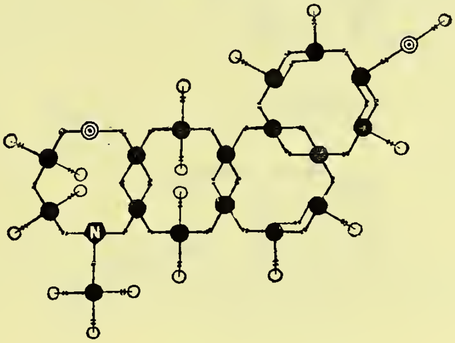


Morphine, $C_{17}H_{19}NO_3$

Here we have phenantrene all right enough; but in order to place the rest a new ring has to be employed containing the oxygen- and nitrogen-atoms. This ring is the morpholine-ring, mentioned before (fig. 1404 A, p. 390). Other investigators (*Monatsh.* x. pp. 101, 732) have objected to the whole structure because in it one methyl only is affixed to the nitrogen, whereas they have found ethyl-methyl-amine amongst the decomposition products from morphine. The matter will be cleared up some day, no doubt, but it does not seem impossible that ethyl-methyl-amine may be split off from such a peculiarly formed structure as the above, where it seems anticipated and almost ready to be formed.

Apomorphine is morphine less a molecule of water. Supposing the above structure correct, the water would most likely be formed from the hydroxyl and hydrogen which have broken the double bond of the morpholine-ring, and apomorphine would then have such structure :

FIG. 1497

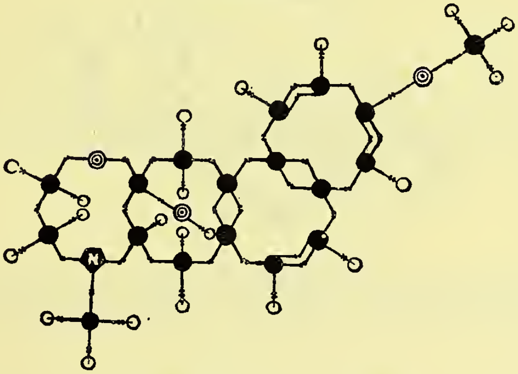


Apomorphine, $C_{17}H_{17}NO_2$

Apomorphine is said to be the 'active principle' in the American Gold Cure for habitual drunkenness.

Codeïne differs from morphine by a methyl joined to the hydroxyl in phenantrene.

FIG. 1498



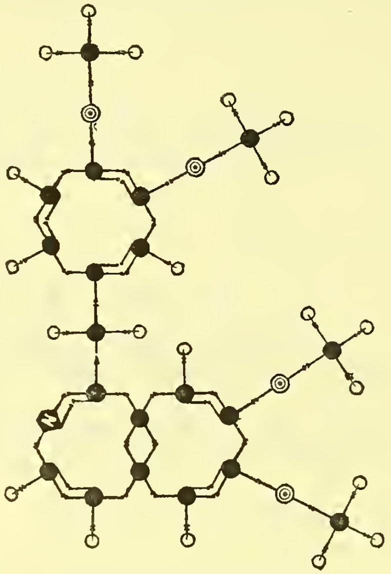
Codeïne, $C_{18}H_{21}NO_3$; m.p. 150°

Codeïne has been prepared by methylating morphine.

Apocodeïne is formed from codeïne by elimination of a molecule of water, probably in the same manner as we have just supposed apomorphine to be formed from morphine.

As regards quantity, the third most important alkaloïd in opium is papaverine. The structure of this compound has been fully accounted for, and may be represented thus (*Monatsh.* ix. p. 781):

Fig. 1499

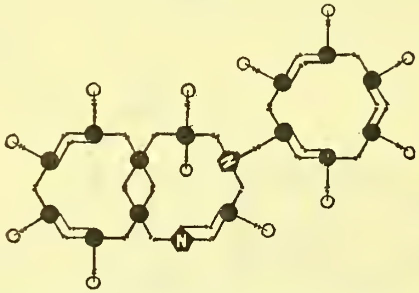


Papaverine, $C_{20}H_{21}NO_4$

This is about all that we know of the structures of alkaloïds.

There is one more compound to mention before we close this chapter, viz. orexine; it is one of the 'modern remedies,' a derivative from quinazoline (fig. 1409, p. 390) by hydrating and joining it to a phenyl:

Fig. 1500

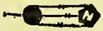


Orexine, phenyl-dihydro-quinazoline, $C_{14}H_{12}N_2$; m.p. 130°; the hydro-chlorate (m.p. 231°) is used as a stomachicum; recently the base itself has been recommended in preference (*Therap. Monatsh.* 1893; *Ph. C.* xxxiv. p. 393)

# CYANOGEN AND DERIVATIVES

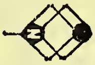
We have seen nitrogen and carbon united by one or two valencies, but they may also be bound together by three valencies, forming cyanogen, or even by four, forming iso-cyanogen.

Fig. 1501



Cyanogen-group

Fig. 1502



Iso-cyanogen-group

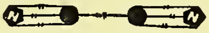
Both, it will be seen, are mono-valent groups, but in cyanogen the free valency belongs to the carbon-atom, in iso-cyanogen to the nitrogen-atom.

There are derivatives from both; with few exceptions they have not found their way into *materia medica*, but we cannot pass them entirely unnoticed, as they are of great importance to chemistry generally.

The cyanogen-group is in all ordinary cases formed by preference, but in the presence of silver the iso-group is formed. This is on all fours with the behaviour of silver towards nitrous acid (*vide* p. 302).

Cyanogen itself is composed of two cyanogen-groups.

Fig. 1503

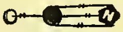


Cyanogen, $C_2N_2$; a gas

It is strikingly like an element, and has many analogies to chlorine; for which reason it is frequently given the chemical symbol Cy.

When a hydrogen is affixed to the cyanogen group, hydrocyanic acid is formed:

Fig. 1504

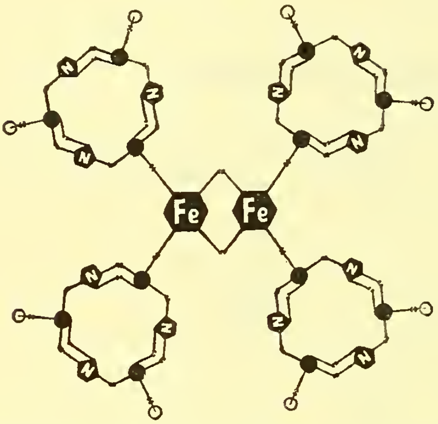


Hydrocyanic acid, HCN or HCy; b.p. 26°·5; occurs in amygdalin, bitter almonds, cherry and laurel leaves; a deadly poison; by substituting metals for the hydrogen, salts are formed, just like hydrochloric acid

The hydro-iso-cyanic acid is not known, neither are any of its salts.

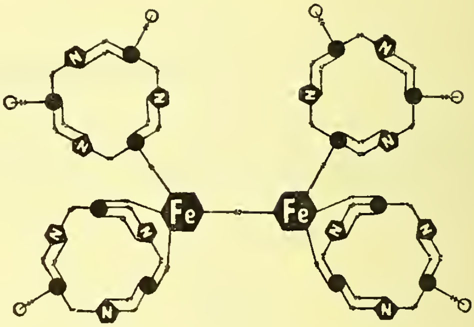
Hydrocyanic acid forms with iron rather peculiar compounds, which combine with potassium-cyanide and form potassium-ferro-cyanide and potassium-ferri-cyanide. Their structures consist of two atoms of iron bound together by double bond in the ferro-compound, by single bond in ferri-compounds; to each iron-atom two rings are affixed, each consisting of three cyanogens, thereby leaving altogether eight valencies free in the ferro-, and six in the ferri-compound, to which either hydrogen, making acids, or metals, making salts, may be joined. This is easily understood from a representation of their structures:

Fig. 1505



Hydro-ferro-cyanic acid, $C_{12}H_8N_{12}Fe_2$; white crystals rapidly becoming blue on exposure

Fig. 1506



Hydro-ferri-cyanic acid, $C_{12}H_6N_{12}Fe_2$; brown crystals; easily decomposed

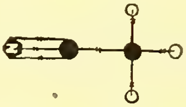
When potassium replaces all the hydrogen-atoms in hydro-ferro-cyanic acid it changes into the salt, potassium-ferro-cyanide, known as yellow prussiate. When the hydrogen-atoms in hydro-ferri-cyanic acid are replaced in the same way, the result is potassium-ferri-cyanide or red prussiate

The molecular weight of these compounds is not known, but in the above figures iron is supposed to be tetra-valent, and, therefore, these structures are probably correct representations of the two compounds. Generally, however, they are for brevity's sake represented by half of these molecules (*e.g.* $C_6H_4N_6Fe$ and $C_6H_3N_6Fe$), whereby iron becomes either a dyad or a triad.

From the two potassium salts, prussian-blue and Turnbull's blue are derived.

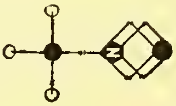
Both cyanogen and iso-cyanogen form derivatives with *alcohol-radicals* (by substituting the hydroxyl of an alcohol). The former are distinguished as nitriles (comp. p. 315) or alkyl-cyanides, the latter as carbamines (*carbyl-amines*) or iso-nitriles (*iso-cyanides*). Thus we have

Fig. 1507



Methyl-cyanide, aceto-nitrile, $C_2H_3N$; b.p. 82°; possesses an aromatic ethereal smell

Fig. 1508

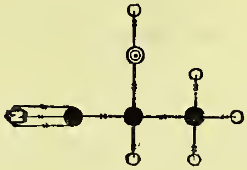


Methyl-iso-cyanide, methyl-carbamine, methyl-carbylamine, $C_2H_3N$; b.p. 58°; unbearable odour

As methyl-cyanide is the nitrile of acetic acid, hydro-cyanic acid may be considered the nitrile of formic acid.

Cyanogen combines also with *alcohols* by substitution of a hydrogen of the latter.

Fig. 1509

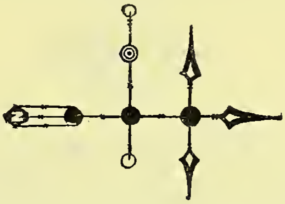


Cyanhydrine, $C_3H_5NO$ ; b.p. 182°

may also be considered the nitrile of ethylidene-lactic acid (fig. 692, p. 179), or of propylene-glycol (fig. 366, p. 77).

When the three methyl-hydrogens are replaced by chlorine, or if cyanogen combines with chloralhydrate (fig. 977, p. 272) by replacing one of the hydroxyls, we obtain

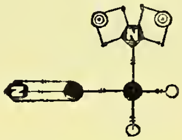
Fig. 1510



Chloral-cyan-hydrine, chloral-cyanhydrate, $C_3H_2Cl_3NO$ ; m.p. 61° ; recommended as substitute for aqua amygd. amar.

If one of the hydrogen-atoms of methyl-cyanide is displaced by a nitro-group (*vide* p. 304), we obtain an acid that forms extremely explosive compounds:

Fig. 1511



Fulminic acid, $C_2H_2N_2O_2$

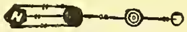
Fulminic acid itself has not been prepared, but compounds in which both hydrogen-atoms are replaced by metals are known. One of them is fulminate of mercury, used in percussion caps.

Several structures, chiefly as iso-nitroso compounds (di-oximes, vide *Ber.* xxiii. pp. 2998, 3505, &c.), have been suggested, but the opinion is at present generally in favour of the above.

Hydroxyl may apparently combine in three different ways with cyanogen and iso-cyanogen; either it may join the carbon atom in cyanogen,

FIG. 1512

No. 1

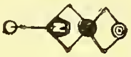


CHNO

or its oxygen may join the carbon, and its hydrogen unite with the nitrogen; two of carbon's valencies engaging the oxygen, the other two remaining with the nitrogen, whose third valency has been set free from its engagement to carbon, and therefore can accept hydroxyl's hydrogen:

FIG. 1513

No. 2

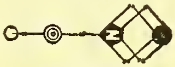


CHNO

A third way for hydroxyl is, of course, to join the nitrogen in iso-cyanogen:

FIG. 1514

No. 3



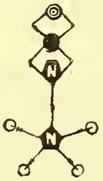
CHNO

The first two must be acids, the third is a sort of hydroxyl-amine which is awaiting discovery. We, however, know but one acid, cyanic acid, and opinions are very much divided as regards structure, whether it is cut on the first or on the second pattern. It will be noticed that the whole difference is the position of the hydrogen-atom, in one it is to the right, in the other to the left, the bonds being obliged to accommodate themselves accordingly. Now, as there undoubtedly are two series of derivatives from cyanic acid, and the atoms in cyanogen compounds appear to possess great migrating aptitude, it is possible that cyanic acid has alternately both forms in quick succession, and that it depends upon the nature of the body it comes into contact with, in which position the hydrogen will finally settle down.

Cyanic acid, whatever its structure may be, is a very unstable body: it exists only at temperatures under zero; at ordinary temperature it polymerises with explosion-like violence into a compound termed cyamelide $(CHNO)_x$.

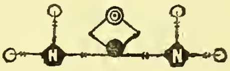
Amongst its salts, one has historical interest, as it was the first brick pulled down from the wall that up to that time (1828) separated *organic* from *inorganic* chemistry. It was the transformation of ammonium-cyanate into urea, effected by Wöhler. This reaction will best be understood when we choose structure No. 2 for cyanic acid.

FIG. 1515



Ammonium cyanate

FIG. 1516



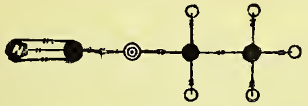
Urea (fig. 1174, p. 328)

The two nitrogen-atoms divide the hydrogen-atoms between them, whereby one of carbon's valencies is set free, and is seized by the rest of the ammonium-group. This intramolecular change is effected simply by heat, and also at ordinary temperatures, but slowly.

Ammonium cyanate may be formed from entirely inorganic bodies, whereas urea is an organic compound, which, like all other organic compounds, was, prior to Wöhler's discovery, believed to be exclusively the product of a special 'vital force.'

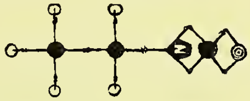
Cyanic acid and alcohol radicals may combine. In these derivatives cyanic acid shows its capability of assuming two structures, some of the compounds being derived from structure No. 1, others from No. 2. The former are true compound-ethers; the latter are not, as will be seen from their structure:

Fig. 1517



Cyanetholine, $C_3H_5NO$; an oily fluid; decomp. on heating

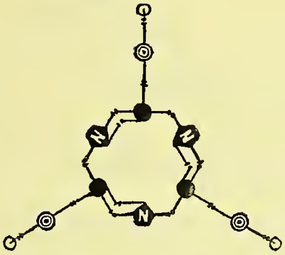
Fig. 1518



Ethyl-iso-cyanate, ethyl-carbonylamine, $C_3H_5NO$; b.p. 60°; of suffocating odour

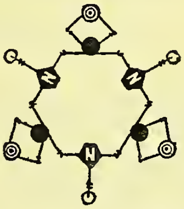
A polymerisation of three atoms of cyanic acid is known and termed cyanuric acid, of which there are two series of derivatives, *cyanuric* and *iso-cyanuric* compounds. The former seems to be derived from No. 1 of the cyanic acid structures, the latter from No. 2:

Fig. 1519



Cyanuric acid, $C_3H_3N_3O_3$

Fig. 1520

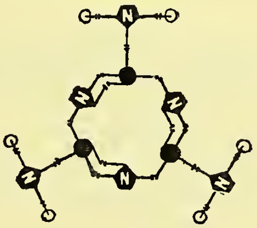


Iso-cyanuric acid, $C_3H_3N_3O_3$

We have met with similar isomers before (comp. phloroglucin, fig. 424, p. 93). Cyanuric acid only is known in the isolated state, but alcohol-radical-derivatives have been prepared from both. The alkyls fix themselves to the hydroxyls in cyanuric acid, and to the imido-group in iso-cyanuric acid, in both cases, of course, replacing the hydrogen-atom.

Amido-groups may replace, one by one, the hydroxyls in cyanuric acid, forming **ammelide**, **ammeline**, and **melamine**, according as one, two, or three hydroxyls are replaced:

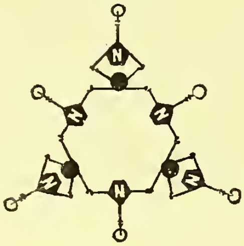
Fig. 1521



Melamine, $C_3H_6N_6$; crystals; decomp. on heating

Derivatives of an isomeric melamine exist, which may be considered derivable from iso-cyanuric acid:

Fig. 1522



Iso-melamine, $C_3H_6N_6$

Iso-melamine is only known through its alkyl-derivatives.

The oxygen in the two structures of cyanic acid may be substituted by sulphur, as we have seen it done, in the previously mentioned thio-compounds (p. 280). We obtain then thio-acids of the following structures:

Fig. 1523

No. 1

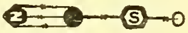
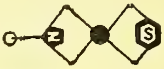


Fig. 1524

No. 2



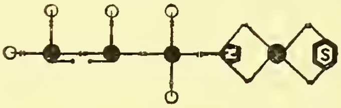
Thio-cyanic acid, CHNS; it is only stable in a freezing mixture

The salts of the first structure are known as rhodanides. The mercury salt, mercurous thiocyanate, which increases enormously in volume upon being burnt, is the substance from which 'Pharaoh's serpents' are made. It is a strong poison.

Two series of alkyl-derivatives are known, one derived from structure No. 1, and another from No. 2, perfectly analogous to the cyanic acid-compounds.

The second class are termed mustard oils, from the fact that the most prominent member, allyl-iso-thiocyanate, is the constituent of the seeds of black mustard, and imparts the pungent odour and taste to mustard. Its structure is

Fig. 1525



Mustard oil, allyl-iso-thiocyanate, $C_4H_5NS$; b.p. 151°

Mustard oil is present in mustard seed as a glucoside (*vide* p. 160), *potassium-myronate*, which, in contact with a peculiar ferment called *myrosin* (p. 446), also present in the seeds, breaks up into sugar, potassium-sulphate, and allyl-iso-thiocyanate; the oil occurs also in horse-radish.

The movability of the atoms in the cyano-compounds and the consequent ease with which they perform intramolecular changes have already been mentioned. This property has made them most valuable assistants in chemical syntheses. Thus it is possible through them to prepare from an alcohol an acid that contains one carbon-link more than the alcohol. For instance, methyl-alcohol containing one carbon-atom may be converted into acetic acid containing two carbon-atoms. It is done in this way: the alcohol is converted into methyl-iodide and brought together with potassium-cyanide, when potassium-iodide and methyl-cyanide are formed, the two exchanging iodine and cyanogen.

Fig. 1526

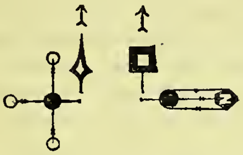


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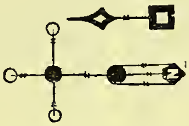
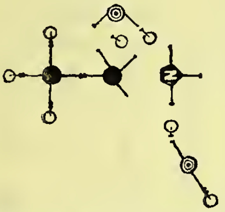
Fig. 1527



Methyl-iodide + potassium-cyanide = Potassium-iodide + methyl-cyanide or aceto-nitrile

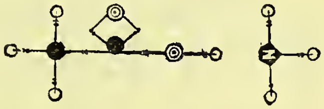
When aceto-nitrile is (super-) heated with water, the nitrogen-atom is split off as ammonia, to which the water furnishes the requisite hydrogen-atoms, the oxygen uniting with the rest of aceto-nitrile to form acetic acid:

Fig. 1528



Aceto-nitrile + two molecules of water

Fig. 1529



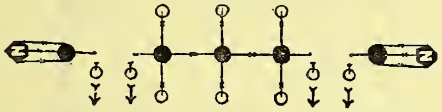
Acetic acid + ammonia

From acetic acid, ethyl-alcohol may be prepared, and from ethyl-alcohol, propionic acid, and so forth.

Such additions of links to a chain are not limited to alcohols and acids; we can add even two links at once to hydrocarbons, by which method piperidine has been formed from propane (actually from a derivative of propane) in this way:

Two cyanogen-groups (of hydrocyanic acid) displace two hydrogen-atoms in propane.

Fig. 1530



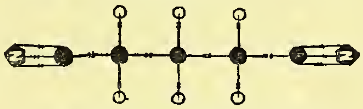
Hydrocyanic acid

Propane

Hydrocyanic acid

=

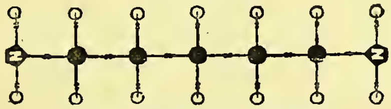
Fig. 1531



Tri-methylene-cyanide, $C_5H_6N_2$; b.p. 274°

Through reducing agents eight hydrogen-atoms are introduced into tri-methylene-cyanide, converting it into penta-methylene-diamine (fig. 1268, p. 357).

Fig. 1532

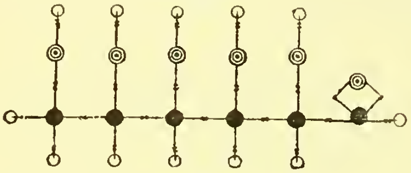


Penta-methylene-diamine

By heating (of its hydrochloric salt), a molecule of ammonia (ammonium chloride) is split off and piperidine is formed, as we have already seen (fig. 1274, p. 359).

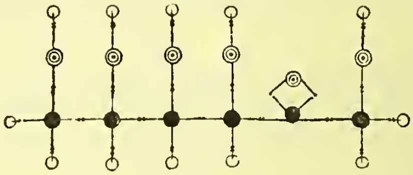
It is to these reactions we owe our knowledge of the structures of the grape-sugar group. When hydrocyanic acid is added to an aldehyde- or a ketone-group, its hydrogen goes to carbonyl's oxygen to form hydroxyl, and its cyanogen group joins the liberated valency, converting the compound into a nitrile, which can again be transformed into an acid as already described. Thus if dextrose and levulose are treated both in this same way, the end-products will be two different acids whose structures are well known, and from which we can draw our conclusion as to the structure of the sugars. The following illustrations will make this easily understood:

Fig. 1533 a



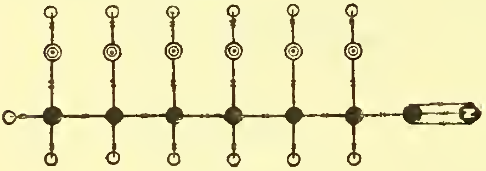
Dextrose

Fig. 1533 e



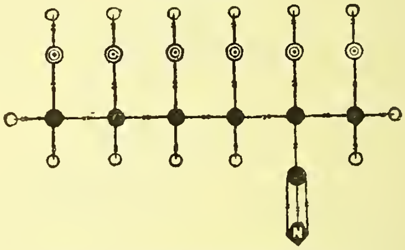
Levulose

Fig. 1533 b



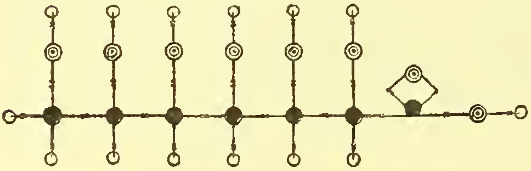
Nitrile of dextrose-carbonic acid

Fig. 1533 f



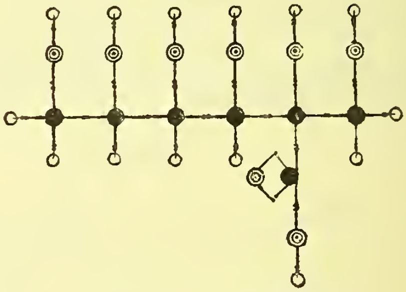
Nitrile of levulose-carbonic acid

Fig. 1533 c



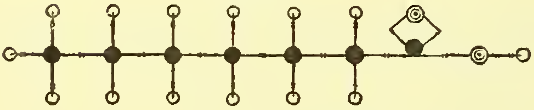
Dextrose-carboxylic acid

Fig. 1533 g



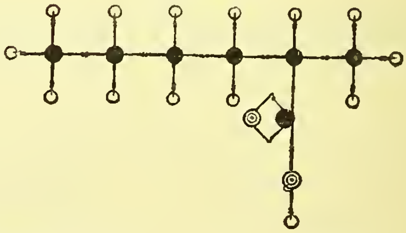
Levulose-carboxylic acid

Fig. 1533 d



Normal heptylic acid; b.p. 223°; solidifies at $-10°\cdot5$

Fig. 1533 h



Methyl-butyl-acetic acid; b.p. 212°; is still fluid at $-20°$

## Future Nomenclature of Cyanogen-derivatives

When a cyanogen-group forms the end-link in a straight chain of a hydrocarbon, the compound is designated as *nitrile*, and, in the case of two such end-links being present, as *dinitrile.* The question of nomenclature for similar side-chains is left open for the present.

Compounds containing an iso-cyanogen-group are termed *carbylamines.*

The name *cyanates* is reserved for the true compound ethers.

Iso-cyanates are termed *carbonimides.*

Thiocyanates (sulphocyanates) retain their names.

Isothiocyanates become thionecarbonimides.

| *Old Nomenclature* | | | *New Nomenclature* |
|---|---|---|---|
| Hydrocyanic acid | (fig. 1504, p. 419) | = | Methane nitrile |
| Methyl-cyanide | (fig. 1507, p. 420) | = | Ethane nitrile |
| Methyl-iso-cyanide | (fig. 1508, p. 420) | = | Methyl-carbylamine |
| Cyanhydrine | (fig. 1509, p. 421) | = | Propane-2 ol-nitrile |
| Fulminic acid | (fig. 1511, p. 421) | = | Nitroethane-nitrile |
| Cyanetholine | (fig. 1517, p. 423) | = | Ethyl- (ethane?) cyanate |
| Ethyl-iso-cyanate | (fig. 1518, p. 423) | = | Ethylcarbonimide |
| Mustard oil | (fig. 1525, p. 424) | = | 1 Propenyl-thione-carbonimide |
| Rhodanethyl | | = | Ethylthiocyanate |

We have now come to the end of our structure-illustrations, and gone through, I believe, so far as the structures have been ascertained, all that can have any interest to medical men. There are, besides those compounds we have discussed, a great many more into which phosphorus, arsenic, selenium, antimony, boron, silicon, zinc, tin, mercury, aluminium, magnesium, &c., have been introduced, and whose structures are well known, but they are more of a specially chemical interest, and need not therefore be mentioned in this treatise. Before, however, we go on to mention the most modern development of the law of the linking of atoms, it may perhaps be useful to give a short summary of some compounds of unknown structure, but in which medical science must be deeply interested, such as proteïds, ptomaïnes, leucomaïnes, and ferments.

# PART XI.

# Proteïds
# Ptomaïnes
# Leucomaïnes
# AND
# Ferments

# Proteïds

Proteïds, or albuminous substances, are the only chemical compounds that we know of existing in the two widely different states, the living and the dead. Our knowledge of the living proteïds amounts to next to nothing. The dead proteïds only have as yet been accessible to examination by the chemist, and what has thus been disclosed is insignificant in the extreme as regards their structure. They are rather stable, but very complex compounds, the smallest possible empirical formula of a dog's hæmoglobin, for instance, being $C_{636}H_{1025}N_{164}FeS_3O_{181}$ (molecular weight 14129), possibly a multiple of these figures. The living proteïds, being in a chronic state of building up and pulling down, have probably an extremely unstable and changing structure, and will split into anything required for the anabolic processes. At the moment of their death they entirely change their chemical character and become the more stable compounds, which have been subjected to scientific research. Physiologists have, indeed, been able to demonstrate under the microscope a reducing power in the living proteïds which is entirely absent in the dead ones. This and some other considerations have led to the hypothesis that the living proteïds partake more of the character of aldehydes, whereas the dead ones have more of a ketonic nature. Some are of the opinion that proteïds are formed from formic aldehyde (fig. 533, p. 130) and ammonia as constituents of aspartic aldehyde ($4CHOH + NH_3 = C_4H_7NO_2 + 2H_2O$; *vide* fig. 1164, p. 326); and that by polymerisation in the presence of sulphuretted hydrogen we should arrive at one of the propounded formulæ of albumin, $C_{72}H_{112}N_{18}SO_{22}$; others consider that living proteïds consist of a chain of cyanhydrines (fig. 1509, p. 421) connected with benzene-nuclei. All this, it should be remembered, is mere paper speculation, with but a very slender base of facts.

We have firmer ground to tread upon when we come to the dead proteïds, though we have not much to be proud of there neither. The great difficulty in all the researches on albuminous substances is that most of them do not form crystalline compounds, nor has any other property been ascertained by which we can determine whether we have to do with a single compound or with a mixture of closely related bodies. Quite recently methods have been found to form albuminous substances into crystallisable compounds by combination with ammonium sulphate (*Zeitschr. f. physiol. Chemie*, 1891, p. 456), and thus we may hope to have in a not distant future more light shed upon these mysterious compounds.

The only chemical way we have had to distinguish between different classes of albuminous substances has been their solubility in different media, and the temperature at which they coagulate. But possibly, and even probably, many of these classes into which we have thus been enabled to divide the proteïds contain more than one compound; the often widely different results to which the several investigators have come, in their ultimate analysis of supposed identical compounds, seem to confirm such an opinion.

Though our knowledge of their structure is *nil*, it may perhaps be useful to take a short view of their behaviour from a chemical and physiological standpoint, as some of their derivatives have become very popular therapeutical remedies, and their names frequently occur, sometimes employed in a not strictly legitimate way, amongst so-called proprietary medicines.

The proteïds are divided into two large groups, according as they are soluble or insoluble in water.

The soluble proteïds are termed **albumins**, the insoluble ones **globulins**. Both coagulate from their solutions through *heat*, which is a distinctly different process from *ferment*-coagulation, and both again from *precipitation*, though the words are often used indiscriminately. A precipitated proteïd preserves all the original character which it had in solution, and may be re-converted into the soluble form. A coagulated proteïd is a new chemical individual which cannot be re-converted into the original substance.

The proteïds consist of carbon, hydrogen, nitrogen, sulphur, and oxygen.

## Albumins

They, like the globulins, are generally divided into animal and vegetable compounds, but as they do not differ in their essential characteristics there is no great necessity for such subdivision. They seem to be very sparingly present in plants, whereas they constitute the chief part of proteïds in the animal organism.

They are distinguished as—

1. **Serum-albumin** which has been prepared from serum. Three different serum-albumins have been distinguished through the different temperatures at which they coagulate.
2. **Egg-albumin** differs from serum-albumin in not being precipitated by ether. There seem to be three sorts coagulating at different temperatures.
3. **Cell-albumin** resembling serum-albumin is found in small quantities in the cells.
4. **Muscle-albumin** is perhaps identical with serum-albumin.
5. **Lact-albumin.** Scum of boiled milk is coagulated lact-albumin.

These are the more important albumins, but quite a number have, besides, been found in small quantities, each supposed to differ in one way or another from all the rest.

Albumin is used as a mordant in calico printing, and therefore prepared on a large scale (chiefly serum-albumin). A solution of albumin mixed with the dye is printed on the cotton; the colour is fixed by coagulation of the albumin through heating.

## Globulins

are insoluble in pure water, and in many concentrated saline solutions, but soluble in the same solutions when diluted. They are the chief proteïds in plants, and are, as such, often met with in crystalline form, in which respect they differ from animal globulins, with which they otherwise have all essential characteristics in common.

The more important and best investigated globulins are—

1. **Fibrinogen**, present in the blood, coagulates at a comparatively low temperature (55°) as a characteristically sticky substance. In the presence of fibrin-ferment (*vide* p. 445) **fibrin** is formed from fibrinogen by another kind of coagulating process. Fibrin is split by pepsin or trypsin into two globulins. There seem to be three varieties of fibrin.
2. **Serum-globulin**, formerly called *fibrino-plastic*, *paraglobulin*, and *serum-caseïn*, consists of a mixture of three globulins:
    - *a.* **Plasma-globulin**, pre-existent in the blood-plasma.
    - *b.* **Cell-globulin**, arising from the disintegration of the white corpuscles and the blood-tablets, is probably identical with the fibrin-ferment.
    - *c.* A **globulin** arising from the formation of fibrin from fibrinogen.
3. **Myosinogen** is a globulin in the muscle-plasm that corresponds, without being identical, to fibrinogen in the blood-plasm. It is coagulated and converted into myosin through myosin-ferment (p. 445) analogous to fibrin-formation. This takes place soon after death, and is

the cause of *rigor mortis.* Besides myosinogen, two more globulins, *paramyosinogen* and *myoglobulin*, are present in the muscle-plasma, but myosin-ferment does not cause them to coagulate.

In plants a globulin is found, very similar to animal myosin: this *vegetable myosin* is believed to be the precursor of gluten-fibrin, which, by the action of a not yet separated ferment—an albumose—forms *gluten* by coagulation. Gluten is, according to one authority, not formed from flour by washing when done at a low temperature (2°), which fact would support the hypothesis of a ferment-action. This has been denied by another authority (*Compt. Rend.* cxvi. p. 202), who has been able to extract 27 per cent. of gluten from flour by water at 0°. Boiling water extracts from gluten a sticky substance called insoluble (*sic*) phyt-albumose (*gliadin, mucedin*); the insoluble non-sticky residue is gluten-fibrin.

4. Vitellin. There is an animal vitellin, ovo-vitellin, and a vegetable one, phyto-vitellin. The latter is distinctly crystalline, and is thus one of the purest proteïds known; still, it leaves an ash of alkaline-phosphates on ignition, and is perhaps a combination of a proteïd with lecithin, in which case vitellin belongs to the nucleo-albumins.
5. Crystallin is the proteïd in the lens of the eye; it is very like vitellin in its properties.
6. Caseïnogen is one of the two proteïds in milk, the other being lact-albumin. It is like a globulin in some respects, but it does not coagulate by heat. With rennet (p. 445) it coagulates, forming caseïn, provided calcium phosphate is present. Caseïn is a nucleo-albumin. French physiologists have stated that the milk of blondes contains less caseïnogen than that of brunettes; this has, however, not been corroborated by other investigators.

Cheese is mainly caseïn with a varying percentage of fats. The ripening is a process of fermentation, or rather putrefaction, brought about by organised ferments. The different varieties of cheese is the result of difference in the bacteria, the various manufacturing places having their distinctive bacteria. Legumin, or vegetable caseïn, is not present as such in plants. It is an alkali-albumin formed from the native globulins by caustic potash, used in extracting it from plants.

A new class of albuminous substances, 'protective proteïds,' also belonging to globulins, are described in connection with toxalbumins and 'immunity,' p. 441.

## COMPOUND PROTEÏDS

Proteïds, complex as they are, combine with other compounds sometimes still more complex. There are several groups of such combinations; some of the better known are nucleo-albumins, glyco-proteïds, and chromo-proteïds.

### Nucleo-albumins

They are widely distributed in animal and vegetable organisms, and consist of proteïds, united to a class of compounds called nucleïns, containing, besides the usual elements of proteïds, always phosphorus, and sometimes sulphur and iron. Cell-nuclei consist of nucleïn.

The opinions about nucleïns are divided; some consider them *mixtures* of organic phosphorus-compounds with proteïds or proteïd-like substances; others are of opinion that they represent *chemical units* in which an albumin forms the nucleus, surrounded by side-groups (*prosthetic groups*) containing all the phosphorus-combinations, which can be split off as *nucleïc acid* by alkalies.

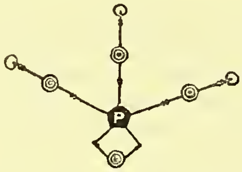
The most important of nucleo-albumins is caseïn, which has already been mentioned.

Amongst the phosphorised constituents of the organism, the most abundant next to nucleïn is lecithin, the only component of vegetable and animal tissues, whose structure has been ascertained. It is a yellowish-white, waxy, hygroscopic solid, which swells and forms a kind of emulsion with water. It is formed from *glycero-phosphoric acid* combined with *fatty acids* and *choline.*

As we have not treated phosphorus-compounds before, it will be necessary to say a little about them now.

Phosphorus is an element that in many of its chemical properties resembles nitrogen. It is a pentad, but, like nitrogen, may also appear as a triad. It forms with oxygen and nitrogen several acids, of which we here have to do with the common *phosphoric acid* only; it differs in its atomic character from the corresponding nitric acid (fig. 1088, p. 306) in this, that it is tri-basic; consequently has three hydroxyls and besides an oxygen-atom tied to phosphorus by a double bond. Phosphoric acid illustrated would, therefore, appear thus:

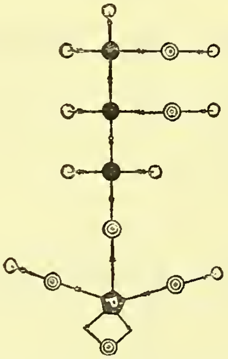
Fig. 1534



Phosphoric acid, $PH_3O_4$

Phosphoric acid combines with glycerin in regular ether-fashion, forming an ether-acid:

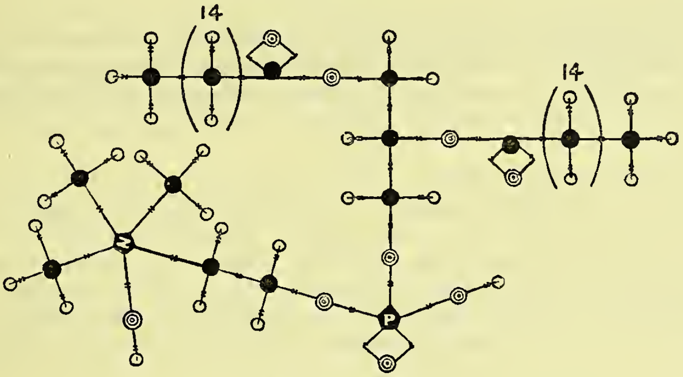
Fig. 1535



Glycero-phosphoric acid, $C_3H_9PO_6$

This is the mother substance of lecithin, which latter is formed by joining radicals of fatty acids to the two remaining hydroxyls of glycerin, and choline (fig. 1260, p. 354), through its alcoholic hydroxyl, to one of the hydroxyls of phosphoric acid. Supposing that the fatty acid-radicals were derived from palmitic acid (fig. 680, p. 177), the structure of lecithin would be illustrated thus:

Fig. 1536



Lecithin, $C_{40}H_{82}NPO_9$

Lecithins have been found which contain stearic acid, others with oleïc acid, others again with one oleïc and one stearic, or palmitic acid-radical, having apparently accepted, or perhaps rather selected, for their formation from such glycerides as were at hand.

Lecithin is nearly ubiquitous: it occurs in the nervous tissues, in the blood-corpuscles, in most organs of the body, in secretions such as semen, bile. milk; in fact, in every growing cell or wherever cellular elements exist. If it is not found isolated it is still present in combination with other bodies. It originates in plants and enters through them the animal organism. It must be looked upon as stored-up capital upon which the organism incessantly draws for supplies of repairing materials, containing, as it does, phosphorus- and nitrogen-compounds, and fats needed for such purpose. It is certainly the intermediate link between the inorganic and organic forms of phosphorus in the mineral and animal kingdoms.

Some similarly constructed compounds are the protagons, found in the brain. Their structure is much more complicated, and contains sulphur besides the constituents of lecithin: carbon, hydrogen, oxygen, nitrogen, and phosphorus. Barium-hydrate splits off from protagons two compounds, *cerebrin* and *kerasin*, probably glucosides. Both contain fatty acids, which are present in cerebrin in the proportion of three molecules to every two atoms of nitrogen. The empirical formula of cerebrin is probably $C_{70}H_{140}N_2O_{13}$, and that of kerasin $C_{70}H_{138}N_2O_{12}$ (*Ztsch. f. physiol. Ch.* xvii. p. 431).

## Glyco-proteïds

are combinations of proteïds and some reducing compounds belonging to the class of carbohydrates or substances easily converted into them. Through the action of dilute acids glyco-proteïds are easily split into these components. To them belong—

Mucins. The best known is that contained in saliva, a slimy substance secreted by the submaxillary gland for the purpose of lubricating the food, thus protecting the pharynx and œsophagus during the process of swallowing.

## Chromo-proteïds

are split into proteïd and pigment.

**Hæmoglobin**, the pigment of the red blood-corpuscles, contains iron, and is crystallisable. It consists of a proteïd, a globin (probably a mixture of proteïds), and a pigment *hæmatin.*

Although it is crystallisable, the analyses of different observers are too discordant to make any probable calculation from them; one, for instance, being $C_{550}H_{852}N_{149}FeS_4O_{149}$, and another, $C_{712}H_{1130}N_{214}FeS_2O_{245}$.

It unites readily with oxygen, molecule for molecule, and gives it off again as easily, acting both as an oxidising and as a reducing agent. It is therefore the great oxygen-carrier of the body, one gramme combining with nearly 1·3 c.c. of oxygen. There is not much of it by weight in each corpuscle, the amount having been calculated to thirty billionths of a gramme, but then there are five millions of corpuscles in every cubic millimetre of blood. The combination of hæmoglobin and oxygen is called **oxyhæmoglobin**, which is formed in the lungs and carried all over the body, where a breathing process is actually performed by the protoplasm in the cells.

From hæmoglobin the pigments of the bile are formed: **bilirubin** (*bilifulvin, cholepyrrhin, biliphæin*), $C_{16}H_{18}N_2O_3$, and **biliverdin**, $C_8H_9NO_2$. Likewise the pigments of urine and fæces.

Other pigments, about which scarcely anything is known, are—

**Lipochromes**, or fatty pigments, such as **carrotin** in carrots.

**Chromophanes** in the eyes of birds, fishes, &c.

**Serum-luteïn**, the pigment in serum.

**Chlorophyll** probably contains lecithin. It has been split into a yellow pigment, *phylloxanthine*, and a blue, *phyllocyanine.* Chlorophyll is supposed to form aldehydes in plants by decomposing the carbonic acid and water present in the atmosphere; and carbohydrates by polymerisation of aldehydes (*vide* fig. 622, p. 153; also fig. 541, p. 132, and fig. 569, p. 139).

**Melanin** is the black pigment produced from hæmoglobin when the red blood-corpuscles are entered and eaten away by malaria parasites; moreover, any black pigment of the body is termed a melanin; sometimes a precursor, **melanogen**, has been found.

## ALBUMINOÏDS

are a class into which all substances are thrown that do not fit any of the classes already mentioned. From a chemical point of view there is scarcely more to do than to enumerate some of them.

**Keratin**, the horny material of the animal body, such as nails, hair, hoofs, &c.

**Skeletins**: *Chitin* occurs in the invertebrate-group.
*Conchiolin* in the shells of gasteropoda.
*Spongin* forms the skeleton of sponges.
*Fibroïn* is the spider's web.
Silk consists of two cylinders, one inside the other; the outer one—
*Sericin*—is removed by boiling water, in which it is soluble; the inner cylinder is fibroïn, or something like it.

**Collagen**, the substance of which the white fibres of connective tissue are composed. The same substance in the bones is termed *osseïn.*

**Gelatin** is produced by boiling collagen with water.

**Elastin** is the substance of which the yellow fibres of connective tissue are composed.

**Spermatin**, the mucin-like substance (but not a mucin) in semen.

Any classification of compounds, about which we know so little as we do about albuminous matters, must necessarily be but provisional and dependent upon the view of their composition taken by individual investigators; there are, therefore, several more or less diverging classifications in existence. The classification worked out in the preceding pages has for its object to place the much concentrated matter before the reader as intelligibly as possible, and has therefore not slavishly followed any individual opinion. For the English view on the matter I am indebted to the excellent work, *Halliburton's Chemical Physiology and Pathology*, from which several quotations for which I could find no happier expression have been borrowed literally. For the way, however, in which these quotations have been used I alone must be held responsible, for which reason these loans have not been specially indicated.

# PHYSIOLOGICAL DE-FORMATION AND RE-FORMATION OF PROTEÏDS

The proteïds are exclusively formed in plants; some of the theories of their formation have already been mentioned (p. 431). From plants they go over into the animal body as dead or coagulated proteïds unfit for absorption and assimilation; therefore they undergo in the digestive organs a process by which they are converted from an indiffusible state (*colloïds*) into a diffusible (*crystalloïds*), depolymerised or, as it were, stripped of their clothes in order that they may be able to slip through the mucous membranes and pass into the circulation. Once on the other side of the membrane they again put on their clothes without delay, perhaps a little altered to suit the new circumstances, and are then ready to be initiated into the mysteries of the protoplasm of the cell, where they receive anew the life which they lost by parting from their mother plant. Such is, in short, the history of the proteïds until they have become assimilated with the protoplasm of cells.

The conversion of indiffusible into diffusible proteïds is, however, performed in several stages. From proteïds they are turned into less indiffusible *proteoses*, and these again into easily diffusible and soluble *peptones*.

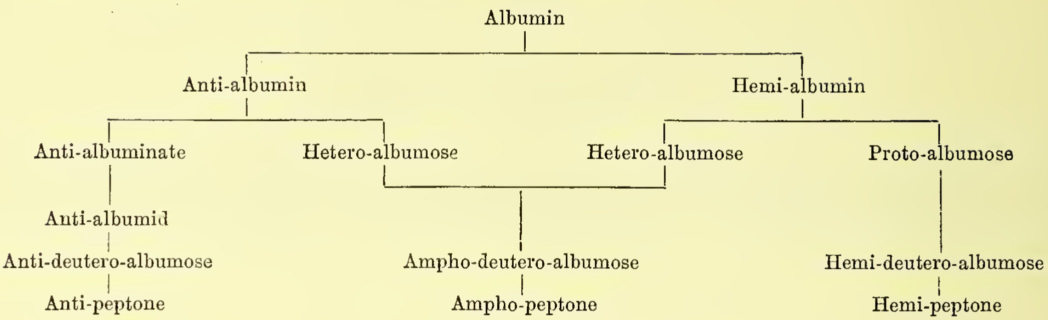
These are only the main features of their transformation, with proteïds and peptones as the beginning and the end. As no collective names have yet been coined for all proteïds in their several stages of transformation, I will select albumin as the body that has been best studied.

Albumins either consist of, or are split by pepsin into, two kinds, anti-albumin and hemi-albumin. Each of them is by the further action of pepsin converted into two different products, of which one is common to both, so that at this stage of the action there are three different compounds: 1, anti-albuminate (*acid-albumin*) [1] from anti-albumin; 2, (hemi-) proto-albumose from hemi-albumin; and 3, hetero-albumose from both. While the last two remain unchanged for a time, the first, anti-albuminate, makes a further step by transformation into anti-albumid. The three substances we now have are therefore: 1, *anti-albumid*; 2, (*hemi-*) *proto-albumose*; and 3, *hetero-albumose.* By yet further action of pepsin these three are converted into 1, anti-deutero-albumose; 2, hemi-deutero-albumose; and 3, ampho-deutero-albumose; and by prolonged action into 1, anti-peptone; 2, hemi-peptone; and 3, ampho-peptone.

---

[1] The same compound (also termed syntonin) is formed by the action of acids upon albumin. Through the action of alkali another compound is formed, called alkali-albumin. Corresponding compounds are formed from globulins. Their collective name is albuminates.

These processes are represented by the following table:—



(From *Halliburton's Chemical Physiology.*)

Anti-peptones are not further acted upon by pepsin or trypsin; they are absorbed by valvulæ conniventes and villi, and during the passage through the mucous membrane of the intestinal wall, or at least on entering the lymph, they put on their clothes (to stick to the homely simile), and appear as regenerated and probably improved albumins, for there are no peptones found in the blood; they, as well as the albumoses, are even strong poisons if they happen to get into the blood unaltered.

Hemi-peptones are further acted upon by trypsin (not by pepsin), being disintegrated into a variety of products, of which the more important are *leucine* (fig. 1160, p. 325), *tyrosine* (fig. 1168, p. 327), *aspartic acid* (fig. 1163, p. 325), *ammonia*, and some compounds of unknown structure.

The other proteïds are similarly acted upon by the digestive ferments and formed into globuloses: *vitelloses*, *myosinoses*, *caseoses*, &c. Many proteïds, albumoses, and peptones are poisonous, those about which we know the least have been collected in one class, toxalbumins (p. 441).

The fermentative action is by some investigators described as a hydration process (introduction of the elements of water), by others as a depolymerisation, but not much is known to support either of these propositions.

As peptones, peptonised milk, meat, &c., have become the fashion of the day, it will be useful to remember that commercial peptones are not peptones at all, but invariably proteoses. The taste of real peptones is extremely disgusting, therefore one cannot expect to find them in the commercial article.

Albumoses are separated from peptones by a concentrated solution of ammonium sulphate, in which the former are soluble, the latter not. The different sorts of albumoses have been recognised and isolated through their solubility in water and in a solution of sodium-chloride; still, they must not be considered distinct chemical bodies, because of their having been entered in the nomenclature as such; in all probability they are mixtures, the chemical character of which may be very different from that of the components. Only very recently (*Monatsh.* xiv. 1893, p. 612) a crystalline compound has been isolated, which seems to be a distinct chemical compound, the first free albumose ever prepared. Insolubility in alcohol has hitherto been considered one of the characteristic properties of albumoses, but this one was soluble; its molecular weight as determined by Raoult's method was surprisingly low, varying from 587 to 714, though the ultimate analysis pointed to upwards of 2000, when calculated on one atom of sulphur as present in its structure.

Hæmatogen is an albuminate present in eggs and probably in most kinds of food, and contains 0·29 per cent. of iron, which is not directly precipitated by ammonium-sulphide.

Ferratin is a similar albuminate found in the liver, derived, no doubt, from hæmatogen, and is supposed to provide the necessary amount of iron required for the formation of the red blood-corpuscles. Commercial ferratin is an imitation of the natural product, and prepared by prolonged reaction of iron-salts on alkali-albumins.

# CHEMICAL AND BACTERIAL DISINTEGRATION OF PROTEÏDS

It has been already stated that the structure of a chemical compound is arrived at by examining the decomposition products, i.e. pulling it to pieces and afterwards trying to get the original compound by putting the pieces together again. Of course that has been tried with the proteïds, and the breaking up has been eminently successful; in fact, not many other organic compounds are so sensitive to chemical agents; and as regards bacterial agents the facility with which albuminous matters break up is simply astounding.

But putting Humpty Dumpty together again is a very different thing, and has not yet been even approached. And do we wonder when the eye runs down the list of fragments comprising almost the whole of organic chemistry as it was known fifty years or so ago?

The following is a list of some of the products obtained by the three agents, destructive distillation, chemical and bacterial actions. The figures refer to the pages in the foregoing treatise, where the structure of the compounds or of similar compounds will be found.

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| Butyraldehyde | 132 |
| Acetone | 138 |
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| Acetic acid | 175 |
| Propionic acid | 176 |
| Valeric acid | 176 |
| Caproïc acid | 177 |
| Palmitic acid | 177 |
| Carbonic acid | 179 |
| Glycollic acid | 179 |
| Lactic acid | 179 |
| Oxalic acid | 184 |
| Succinic acid | 185 |
| Acrylic acid | 190 |
| Crotonic acid | 190 |
| Oleïc acid | 192 |
| Fumaric acid | 195 |
| Benzoic acid | 211 |
| Phenyl-acetic acid | 212 |
| Hydro-cinnamic acid | 212 |
| Phenyl-propionic acid | 213 |
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| | PAGE |
|---|---|
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| Nitro-benzoic acid | 306 |
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| Alanine | 325 |
| Aspartic acid and its homologue, glutamic acid | 325 |
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| Pyridine bases | 391 |
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| Ptomaïnes &c. | 440 |

Visitors to the British Museum are generally shown the Portland Vase as a masterpiece of high-art patch-work. I wonder what the artist would have made out of the above pieces—scarcely albumin.

# Ptomaïnes and Leucomaïnes

Ptomaïnes and leucomaïnes may be called animal alkaloïds in contradistinction to vegetable alkaloïds. As we have no strict definition of the latter there is still less any of the former. Vegetable alkaloïds are generally spoken of as compounds of basic and poisonous character, with a nucleus of pyridine, i.e. cyclo-ammonia-bases, but there are alkaloïds said to be only distant relations of pyridine, *e.g.* morphine and codeïne. Of the constitution of animal alkaloïds we know but little; those few of which we do know the structure are either ammonia-bases with open chains or ammonium-bases, formed from the urea-groups; but to build any definition upon these solitary facts would be premature.

Ptomaïnes and leucomaïnes have been described as basic compounds produced in the tissues of animals, the former being products of abnormal life-processes (exchange of material, Stoffwechsel) in diseases, or the result of bacterial agency after death,[1] the latter produced during life by normal metabolic processes. But as many of them are common to both processes, no sharp line can be drawn in this way. Some are virulent poisons, others quite innocuous, but it would not materially assist us if we were to make poisonous nature the line between them, as most ptomaïnes are poisonous, and many leucomaïnes likewise, even when passing through the alimentary tract. The difficulty is made still more acute by the fact that there are many compounds which can go all the way through the digestive organs without doing any harm, but are deadly poisons if injected into the blood-circulation; and the same substance may frequently, by different authors, be styled a ptomaïne, a leucomaïne, or a toxalbumin, sometimes even by the same author, and it is quite a common thing to write about ptomaïnes produced by bacteria, in anthrax, puerperal fever, hydrophobia, &c., and formed during life.

The safest thing to do in present circumstances is to simply enumerate these compounds as ptomaïnes and leucomaïnes without giving any reasons for such classification. The empirical formulæ if known will be added, though it is only a poor idea of their constitution which they suggest, and some may be liable to correction.

## Ptomaïnes

We have already mentioned those whose structures are known, viz.—

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| Propyl-amine, | fig. 1110, p. 313 | Betaïne, | fig. 1265, p. 355 |
| Di-methyl-amine, | fig. 1115, p. 314 | Putrescine, | fig. 1267, p. 357 |
| Tri-methyl-amine, | fig. 1121, p. 315 | Cadaverine and neuridine, | fig. 1268, p. 357 |
| Tyrotoxicon, | fig. 1213, p. 337 | Methyl-guanidine, | fig. 1336, p. 374 |
| Choline, | fig. 1260, p. 354 | Collidine and hydrocollidine (copellidines, p. 397), | fig. 1418, p. 392 |
| Neurine, | fig. 1261, p. 354 | Parvoline, | p. 393 |
| Muscarine, | fig. 1262, p. 355 | | |

Unknown structures: Saprine, $C_5H_{16}N_2$; tetanotoxine, $C_5H_{11}N$, secretion from bacillus tetani; tetanine, $C_{13}H_{30}N_2O_4$, from the same bacillus; typhotoxine, $C_7H_{17}NO_2$, from the typhus bacillus; mytilotoxine, $C_6H_{15}NO_2$, the poison in mussels; gadinine, $C_7H_{16}NO_2$, from putrid cod-fish. In cod-liver oil, prepared from putrefied liver, several ptomaïnes were found: butylamine, iso-amylamine, hexylamine, $C_6H_{15}N$; di-hydro-lutidine (comp. p. 393); asseline, $C_{25}H_{32}N_4$; and morrhuine, $C_{19}H_{27}N_3$, all of which are bacterial decomposition-products from albuminous substances in the cells and connective tissues of the putrid liver, perfectly analogous to cheese and sausage poisons; consequently ptomaïnes and not leucomaïnes from the bile, as demonstrated in my '*Concluding Remarks*' in the first part of this book.

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[1] Ptomaïnes do not always appear to be directly produced by bacteria, but through the action on albuminous substances of a ferment-enzyme discharged by them.

## Leucomaïnes

The difficulty met with in an enumeration of compounds which may be considered under this head is, as I have said before, to draw the line. A great number may be included, or but a few. I will give the names of the few, proceeding as before.

Creatinine (fig. 1339, p. 375); xanthine (fig. 1347, p. 376); hypoxanthine or sarcine (fig. 1348, p. 377); adenine (fig. 1349, p. 377); guanine (fig. 1351, p. 377); carnine, $C_7H_8N_4O_3$, supposed to be *di-methyl-urea*; pseudoxanthine, $C_5H_4N_4O_2$, isomeric with xanthine, two carbon-links and a nitrogen-link exchanging places (others give the formula $C_4H_5N_5O$, in which case it is, of course, not an isomer of xanthine); para-xanthine, $C_7H_8N_4O_2$ (isomeric with *theobromine*, fig. 1352, p. 378); xantho-creatinine, $C_5H_{10}N_4O$; cruso-creatinine, $C_5H_8N_4O$; amphi-creatinine, $C_9H_{19}N_7O_4$; samandarine, $C_{68}H_{60}N_2O_{10}$, the basic poison of the salamander; most of them have been separated from muscle, some also from urine and fæces.

During waking hours some leucomaïnes of a soporific nature are said to be formed, and during sleep others, which are stimulants; thus when a sufficient amount of the first sort has accumulated we get sleepy; the others make us wide awake. Physiologists have several other, of course non-chemical, theories. They are all about equally well founded.

### Toxins and Antitoxins

Besides the basic compounds just described as originating from normal and abnormal processes in the organism, some albuminous substances owing their existence to the same causes have also been discovered. Some of them, poisonous, are termed toxins or toxalbumins; others protect the organism against the activity of the former, and are therefore termed antitoxins.

Amongst toxins produced by normal life-processes may be named: Snake-poisons (cobra, viper, crotalus, copperhead, and moccasin); abrin, a poisonous proteïd (consisting of a globulin and an albumose), from the fruit of *Abrus precatorius* (jequirity); ricin, a proteïd from the seeds of *Ricinus communis*.

Toxins abnormally produced in the organism by bacterial activity are, for instance: Anthrax-proteïn, from the anthrax bacillus; toxo-peptone and toxo-globulin, from the cholera bacillus; toxo-mucin, from bacillus tuberculosis; in several instances arrow-poisons have been recognised as albuminous substances, and belong probably to this class. The toxic properties of toxins in solution seem to be destroyed if exposed for some ten hours to the sun's rays, or for a couple of hours to a constant electric current, but no such effect is produced upon the dried toxins by these agents. The toxins are supposed to be the real cause of the various diseases from which the bacilli derive their names; but it has been found that some organisms are able to kill certain bacilli or neutralise the poisonous toxins which they produce; for instance, negroes are proof against the bacillus of yellow fever, and so are rats against *vibrio Metschnikowi*: this state of the organism is called *immunity* as regards that disease, and recent researches have established the presence of albuminous substances in the blood of such animals, which are believed to protect the organism against the diseases that the respective bacteria otherwise would have caused. It has further been ascertained that pathogenic bacteria themselves produce, besides their particular poison, an albuminous substance which, if separated and injected into the blood, protects the organism in a similar way. When an animal has been thus made immune, it has been found that the blood-serum of such animal, when injected into the circulation of another, makes this second one also immune; even milk from the first, subcutaneously injected into other organisms, is sufficient to produce immunity; further, it appears that one animal can at the same time be made immune against several diseases by simultaneously injecting the secretion of different bacteria; the blood-serum or milk of this animal will then, by injection, make another, proof against all the diseases ordinarily produced by the respective bacteria employed.

These albuminous substances, whether found as normal products or created artificially in the blood, are distinguished as antitoxins, protective proteïds, vaccines, or alexines; physiologically they have been divided into sozines, those found in animals naturally immune, and phylaxines, those found in animals which by subcutaneous injections have artificially been made immune.

Sozines are again divided into mycosozines, which protect by killing the bacteria, and toxosozines, which act as antidotes to the poisonous excretions of bacteria.

Phylaxines are similarly divided into mycophylaxines and toxophylaxines, according as they destroy bacteria or their poison.

Sozines seem to live in the cells, whereas phylaxines are apparently in solution in the liquids of the organism (*Centralbl. f. Bakteriol.* 1891, x. pp. 337, 349, 377).

Several antitoxins have already been prepared, though not in the isolated state. Of phylaxines may be mentioned: Tuberculin and the purified products tuberculocidin, tuberculinic acid, tuberculinose, and antiphthisin, from bacillus tuberculosis; malleïn, prepared from glanders; antidiphtherin, from the diphtheria bacillus; antitoxin, from the typhus bacillus; anticholerin, from the cholera bacillus; cancroïn (from the supposed cancer bacillus) is now considered identical with neuridine, a ptomaïne. Amongst sozines may be counted: Cardin, extracted from the heart-muscles of cattle; cerebrin, from the brain; sequardin, from the bull's testes (comp. spermine, p. 358); nucleïn, from the spleen of calves. The investigations on toxins and antitoxins are quite in their infancy, groping in the dark; the importance of supposed discoveries is generally grossly over-estimated by the discoverer and his followers, and the anxiety to be the first in the field leads to so many badly founded and foregone conclusions that the above representation of the present state of this part of the science will probably be of little value in a short time.

# Ferments

Under the collective name of ferments are classed a large number of bodies of which chemically we know nothing except that, without, themselves, apparently undergoing any chemical change whatever, a small quantity may affect the constitution of a large quantity of certain other chemical compounds.

Some of them are living organisms, others chemical compounds; but the action of both is of the same nature, viz. breaking up larger molecules of those compounds with which they come in contact into smaller molecules; each ferment has, as a rule, the power to act upon but one special class of compounds, and in cases where more ferments have the power of acting upon the same compound, they generally do so in different ways.

They are divided into two large groups: 1, organised ferments, and 2, unorganised ferments or enzymes.

## ORGANISED FERMENTS

comprise a large number of the lowest class of plants, unicellular organisms, belonging to fungi, such as torulæ and bacteria. Their action upon chemical compounds is called fermentation, which term also includes the action of unorganised ferments.

They are chemically classified according to the sort of fermentation they produce; the principal of these are: 1, *alcoholic*; 2, *acetic*; 3, *lactic*; 4, *butyric*; and 5, *mucous* fermentation. Of course bacteriologists have several classifications of their own.

From a chemical point of view there is not much more to say about this group, without going too far into details, except it may perhaps interest some to know—nervous people, beware!—that, with every mouthful of bread-and-butter, we swallow as many microbes as there are inhabitants in Europe—say three to four hundred million.

## UNORGANISED FERMENTS

are true chemical compounds, the product of the activity of living cells. Their constitution is entirely unknown, none of them having as yet been isolated in a perfectly pure state. They resemble, however, in many respects the proteïds, which, as we now know, is not saying much; indeed, our wisdom may be put into a nutshell: some ferments have been recognised as aldehyde-like compounds.

In the absence of any knowledge of their chemical constitution they also are classified according to the effect they exert upon other compounds, and may consequently be divided into—

1. *Proteolytic* ferments, which change proteïds into peptones.
2. *Amylolytic* ferments, changing amylose (starch &c.) into sugar.
3. *Inversive* ferments, converting cane-sugar into glucose.
4. *Steatolytic* ferments, splitting fats into fatty acids and glycerin.
5. *Coagulative* ferments, converting fibrinogen, caseïnogen, myosinogen, &c., into fibrin, caseïn, myosin, &c.
6. *Glucoside-splitting* ferments, splitting glucosides into glucose and other compounds.

## Proteolytic, Proteo-hydrolytic Ferments

All unorganised ferments are formed in the secreting cells of the living organism, selecting from the lymph certain materials, which are worked up by the protoplasm of the cell into a secretion termed zymogen, and discharged into the lumen of the gland of which it forms part. During the discharge this zymogen is converted into the ferment zyme or enzyme, which is the ferment that acts upon the proteïds. Sometimes the ferment is formed without its precursor zymogen, or, may be, the latter has as yet escaped detection.

We shall mention some of these ferments and their precursors.

Pepsinogen is formed in both the pyloric and the cardiac glands of the stomach. On leaving the cells it is converted into a proteïd pepsin, and is as such discharged into the stomach. Pepsin converts the non-absorbable proteïds through a series of intermediate products, proteoses, into the absorbable peptone; it can, however, do so only in the presence of an acid. In the stomach this acid is hydrochloric acid, which is produced by the parietal cells of the cardiac glands. The discharge from the glands into the stomach is, as a whole, called gastric juice, which, however, contains other ferments than pepsin.

Trypsinogen is formed in the pancreas cells and leaves them as trypsin, which is discharged into the duodenum. It acts similarly to pepsin on proteïds, but more rapidly and best in an alkaline solution, and also, but not so well, in a neutral one; it will not act at all in an acid medium, and is destroyed by hydrochloric acid. Salicylic acid does not hinder the action of the ferment. The discharge from the pancreatic gland is alkaline, and called pancreatic juice: this contains also other ferments besides trypsin.

Papaïn or papayrotin, obtained from the juice of the papaw plant (*Carica papaya*), also from figs and melons, converts animal proteïds into proteoses, and finally into peptones. It works in a neutral medium, but best in a slightly alkaline solution; the smallest quantity of hydrochloric acid is inhibitory, and papaïn therefore cannot be used as a substitute for pepsin. Vegetable proteïds are not converted by it further than into proteoses. Papaïn is only one instance of proteïd-splitting ferments occurring in plant tissues; probably such ferments are present in all, especially in carnivorous plants; one has been found in pineapples, which, unlike papaïn, acts in a slightly acid solution, and is rendered inactive by alkalis.

Pepsin and pancreatin (the dried gastric and pancreatic juices from animals, such as pigs, sheep, or calves) are now prepared on a large scale. Pepsin acts probably as a carrier of hydrochloric acid, and, having delivered the acid to the proteïd, is regenerated into pepsin, ready to serve again as carrier. A small quantity of perfectly pure pepsin should be able to convert an unlimited quantity of proteïds into peptones; none so pure has as yet been prepared, but immense improvements have taken place. Pepsin that will dissolve 10,000 times its own weight of albumen, or even more, is already prepared (*Sitzung d. ph. Gesells.* in Berlin, February 2, 1893; *Ph. C.* **xxxiv.** p. 92). The requirements of the *B.P.*, 1885, were satisfied with 1 : 50.

## Amylolytic Ferments

Ptyalinogen is the ferment-precursor formed in the three salivary glands, the parotid, the submaxillary, and the sublingual. Ptyalinogen appears in saliva as ptyalin, a ferment that converts starch into dextrin, maltose, and some glucose; it has no action upon cellulose, consequently none on uncooked starch-grains, and an acid stops its activity altogether. The influence of saliva upon the secretory and motory action of the stomach is greater when it has been mixed with the food in the mouth before it enters the stomach than when separately brought there through a tube (*Zeitschr. f. klin. Med.* xxi. pp. 1, 2).

Amylopsin is a ferment discharged together with trypsin from pancreas. It has the same action as ptyalin upon starch, converting it into maltose, and by some investigators is considered identical with it. It is not indispensable to the digestion and resorption of carbohydrates, but it has been experimentally demonstrated that grape-sugar is carried off through the urine in its entirety without any transformation after extirpation of both the salivary glands and the pancreatic gland.

Diastase, a proteïd, is a ferment always present in small quantities in plants, but specially abundant in seeds during germination. There seems to be two forms of diastase: *translocation-diastase*, which acts by dissolving the starch-grain evenly, and as a whole; and *diastase of secretion*, which eats away the starch-grain in a very irregular manner; both, like ptyalin, convert starch into sugar.

## Inversive Ferments

Invertin (*invertase, zymase*) is extracted from certain kinds of yeast. It splits cane-sugar into dextrose and levulose.

Glucase is present in non-germinating seeds in a soluble form. It converts dextrin into dextrose.

Succus entericus contains one or more similar ferments, converting cane-sugar into dextrose and levulose, maltose into glucose, milk-sugar into dextrose and galactose. This class and the amylolytic ferments are sometimes lumped together under the name of carbohydrate enzymes.

## Steatolytic Ferments, or Glyceride-enzymes

Steapsin.—The existence of this ferment is inferred from the action of pancreatic juice on fats. It has never been isolated.

Seeds contain similar ferments, which during germination split up the oils in them; such ferments have been found in the seeds of rape, poppy, hemp, maize, and *Ricinus communis.*

## Coagulative Ferments

Their action is probably not always to break up but often to build up, either from two different compounds or by polymerisation from one compound.

Fibrin-ferment is derived from the disintegration of the white blood-corpuscles and tablets after the blood has left the organism, and is probably a globulin. The addition of this ferment to fibrinogen causes the formation of *fibrin* by coagulation.

Myosin-ferment corresponds exactly to fibrin-ferment, causing in the same manner the formation of *myosin* from myosinogen, a proteïd found in the muscle. Myosin-ferment is probably an albumose.

Rennet (*chymosin*) is a similar ferment, formed together with pepsin in the pyloric and cardial glands, and together with trypsin, amylopsin, and steapsin in pancreas. It is generally prepared from the mucous membrane of the fourth stomach of the calf; several plants contain ferments, which have a great resemblance to rennet, and in some localities are used for curdling milk.

Through the action of rennet a soluble proteïd present in milk, called caseïnogen, is converted into the insoluble proteïd caseïn (curdling or clotting milk).

Gluten-ferment, hypothetical, is supposed to convert some pre-existent proteïds in flour into gluten.

## Glucoside-splitting Ferments

Emulsin, or *synaptase*, present in bitter almonds, will split several glucosides; thus *amygdalin*, a compound occurring in bitter almonds, is split up into oil of bitter almonds, hydrocyanic acid and glucose; *salicin*, found in varieties of salix, into saligenin and dextrose, p. 160; *coniferin* into coniferyl-alcohol and dextrose (*ibid.*); *æsculin* into æsculetin and dextrose (*ibid.*), &c.

Myrosin, found in the seeds of black and white mustard, and in *cruciferæ* generally, breaks potassium myronate up into *potassium bisulphate*, *mustard-oil*, and *dextrose* (p. 424). It is peculiar inasmuch as it does not require the presence of water in the reaction.

There are many other enzymes of which we know little more than their existence, for instance:

Histozyme in the kidneys splits hippuric acid into benzoic acid and glycocoll, which seems strange when we remember that hippuric acid is formed when carnivorous animals (including man) are fed upon benzoic acid (p. 330).

By torula ureæ is produced an enzyme which transforms urea into ammonium carbonate.

The anthrax bacillus produces an enzyme that forms albumoses from fibrin.

The cholera bacillus is the origin of an enzyme, which forms sugar from starch, peptonises proteïds, and coagulates milk &c.

# PART XII.

# Atoms

# A CHAT ABOUT ATOMS

We have now handled atoms and molecules so long that curiosity may be excused when raising the question, what they really are, and what they look like. Well, no one has ever seen, or will ever see, them, so it seems a rather hopeless question to put; still human ingenuity is great, and it is almost incredible what wonderfully constructed fabrics it can build from a few bricks of facts. We will give them a short review.

It is well known that gases expand when the temperature is raised, and contract if it be lowered, and it has been ascertained that all gases expand or contract equally at equal changes of temperature. This dilatation or contraction has been found to be a constant fraction of its volume for each degree of altered temperature, and that this constant is $\frac{1}{273}$ of the volume of any gas. Suppose, then, we have a gas which at 0° measures 273 units of volume, it would at $-1°$ measure 272; at $-2°$, 271 units; and at $-273°$ (which temperature is termed the absolute zero) its volume would be 0, provided the law holds good at all temperatures. It has, therefore, been said that atoms were nothing but motion, which at $-273°$ would cease, and matter would vanish like a ball in a conjurer's hand—only more thoroughly.

This theory has not met with general approval, as there are a good many well-founded objections to its acceptance, amongst others that the above law is applicable only within narrow limits.

The most recent theory of atoms is the so-called vortex hypothesis. Besides the matter we can see or feel, other matter is supposed to exist, filling the whole space, but not accessible to our senses. The necessity of assuming its existence is a consequence of the nature of forces. If a force acted on a body at a distance, without any intervening medium, the action would be instantaneous, i.e. not occupying any time for traversing the intervening space. But ever since the days of Römer, we know that light takes time to travel through space; and lately it has been shown that electrodynamic action also requires time, and, indeed, the same time as light for its propagation from one point of space to another. This can only be explained by the existence of a medium, which has been called the ether. It is a rather funny sort of matter, which, though material, does not possess the properties of ordinary matter. It is neither a gas, nor a liquid, nor a solid; still it has at the same time something of the nature of these three: it has penetrability like a gas, only in an infinitely higher degree, as it pervades everything, gases, fluids, and solids; it has mobility like a fluid in so high a degree that it may be regarded as a perfect fluid, i.e. one which is entirely devoid of internal friction, an ideal fluid which does not elsewhere exist in nature. Finally, it has one property exclusively belonging to solids, viz. rigidity; a thousand millionth of that of steel, it is true, still rigidity; and its density is, as an offset, a hundred trillion times less than that of steel. Such is the ether, if there be any at all.

In and from this ether it is that the atoms have been formed by it having 'once upon a time' been set in rotatory motion; and once set rotating it will always remain so, since there is no internal friction. The rotating parts of the ether, or vortices, as they are called, are, if singly, the atoms, or, if linked, the molecules. A smoke-ring, such as some tobacco smokers can produce to perfection, is an illustration of a simple circular vortex-atom. An apparatus which produces these smoke-rings from ammonium chloride has been constructed in order to study their properties. When a ring is sent out of the apparatus it advances revolving—as a string will do when rolled between the fingers—with diminishing speed, on account of friction with the air, and growing in size until it stops and disappears. But if a second ring be projected directly after the first, in a slightly diverging direction and at a somewhat greater speed, it will, of course, overtake the former, but they will not collide; they will move alongside each other, vibrating like an elastic ring after an impact. If the second ring is sent off exactly in the same direction, it will, when approaching the first, grow smaller, and finally pass through if it has sufficient speed; if not, they will remain one inside the other, both revolving all the time, representing a molecule in the ether, while a single ring represents an atom.

The rotatory motion of the rings produces in the surrounding ether corresponding currents, which, following the direction of the rotation, flow forwards through the interior of the ring and backwards on the outside, like the wire round an electro-magnetic ring; these currents then represent the sphere of action round an atom or a molecule, and give a ready explanation of the phenomena mentioned above. Thus the second ring remains inside the first, because the current on the outside of one vortex is opposite to the current on the inner side of the other, the speed of both being equalised. It is on account of the same currents that actual collision between two molecules is prevented, and that the division of an atom or ring is impossible, because nothing can come near enough to touch it in a perfect fluid like the ether.

We have before discussed the three different states of matter, and need therefore only repeat that these vortices have the two motions specified in describing the smoke-ring, a revolving and a forward motion. In the solids, where the vortices are sufficiently close for the currents to touch each other, the forward motion is, as a consequence, changed into another sort of revolving motion, one vortex (or combination of vortices) whirling round another. When solids are converted into liquids the proximity is not so great, although the revolving motion is continued, and more freedom therefore is allowed to the individual molecules, though, surrounded as they are on all sides by other molecules, they cannot entirely free themselves, and resume their straight path except on the surface, where escape is possible for some of the molecules, which process we call evaporation.[1] Some of these released molecules will collide and be thrown back into the liquid (condensation), and the number of these increases with the number of escapes. When just as many are thrown back as escape, the space above the liquid is said to be saturated.

In the gaseous state the vortices are removed from one another far beyond the influence of their currents (sphere of action), and therefore resume their original straight paths in all directions. A consequence is that they frequently collide and rebound like two billiard balls, and comparatively few reach the boundaries of the gas to exert, through their impacts, the gaseous pressure upon the walls of the enclosing vessel. These collisions prevent a joint and simultaneous attack of the molecules, which would be disastrous to whatever might happen to be in their way. It has been calculated that if all the molecules of the air inside an ordinary room could be directed in parallel paths, there would be exerted a sudden pressure of several thousand horse-power—sufficient to shatter the walls into atoms. If we possessed handy means to effect this change of direction—something like the 'Vril Staff' in the convenient form and size of a walking stick, as described by Bulwer in *The Coming Race*—there would be good reasons for the nations to disarm, and excellent prospects for the 'eternal peace.' As it is, revolvers, guns, cannon, dynamite, and other crude arrangements, working upon the same principle, have proved insufficient for the purpose, or worse than that.

The movements of the atoms or molecules are very rapid, and their size is so minute as to be almost beyond conception. A gas molecule moves at a speed of over 500 yards per second; that is, the same as that of a rifle bullet or a point in equator. Although rapid enough, still it is not much compared to that of light and electricity (when propagated through space), which is 40,000 miles per second. But the collisions of a molecule with others are 5,000 million per second, and it passes by sixty-two other molecules between each collision, or more than 300,000 million per second, and the length of the path it travels from one collision to another (*the mean free path*) is $\frac{1}{250,000}$ part of an inch. The diameter of a molecule, including the sphere of action (there may, of course, be considerable difference in size of the molecules of various compounds depending on their complexity) is $\frac{1}{125,000,000}$ part of an inch, and their mutual distance from sphere to sphere in a liquid, *e.g.* water, is calculated to $\frac{1}{1,250,000,000}$ part of an inch, i.e. $\frac{1}{10}$ of their diameter, whereas in gas the distance is eighty times greater, or eight times the diameter. In a cubic inch of air there are over 4,000 trillions of molecules, and in what we are pleased to call the vacuum of our best air-pumps there are still nearly 400 billions of molecules in every cubic inch. In this connection we may mention that there are more than 40,000 million cells in a cubic inch of beer, and in order to convert one grain of grape-sugar into half a grain of alcohol, no less than 150,000 millions of cells are required, each composed of a great number of atoms.

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[1] Such evaporation also takes place in solids, but to so slight an extent that we need not consider it here (comp. p. 279).

When we know the size of an atom, it is of course easy to calculate its weight, the specific gravity being known. In the case of hydrogen we find thus that an atom weighs 0·000,000,000,000,000,000,000,004 gramme, i.e. one quadrillion of hydrogen-atoms weighs 4 grammes = 60 grains.

When we are airing billions, trillions, or even if it be only figures not much above what a millionaire may boast, we scarcely realise what we are talking about, and I dare say the above figures have not left much of an imposing impression upon the reader's mind. In order to appreciate such figures they must be presented in a way that strikes home, for which purpose we can with advantage use the intuitive principle of instruction, the idea of which is taken from *Nature*, 1870, p. 553.

If we take a drop of water as large as a pea, with a diameter of, say, sixteen millimetres (0·6 inch) and imagine it growing, the molecules also growing proportionally, then when the drop has reached the size of the earth, the molecules would be larger than small shot, but not so large as a cricket ball.[1] They would, if in stationary position, stand with their surfaces (taking the medium size between small shot and cricket balls) $\frac{1}{3}$rd of an inch apart, filling the whole globe. If this drop of water, grown to the size of the earth, were converted into gas (steam) it would form a globe, the surface of which would touch the moon, the size of the molecules remaining unaltered, the mean free path which the molecules would traverse in $\frac{1}{60}$th of a second would be about four yards, and their mutual mean distance from centre to centre about two feet.

Magnified ten million times, the dimensions might be conveniently measured by millimetres;

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[1] The distance between molecules in gaseous state (at 0° and at the pressure of one atmosphere) is $\frac{160}{10^8}$ mm., measured between their centres. If we imagine 1 mm.$^3$ of gas divided into cubes, the sides of which are equal to this distance, we find the number of molecules in 1 mm.$^3$ gas $= 2{\cdot}44\ (10)^{17}$. 1 mm.$^3$ of air weighs $\frac{1{\cdot}293}{10^3}$ m.g.; and if $m =$ the molecular weight ($H_2 = 2$), then one molecule of a gas weighs $\frac{1836 \cdot m}{10^{25}}$ m.g. If $\gamma$ is the specific gravity of the molecule relative to water, then the diameter of the molecule $= \frac{7}{10^8} \sqrt[3]{\frac{m}{\gamma}}$ measured in mm. ($\frac{m}{\gamma}$ = molecular volume). If we now magnify as proposed, the diameter of the molecule will be $56 \sqrt[3]{\frac{m}{\gamma}}$ mm.

What value has $\gamma$ or $\frac{m}{\gamma}$? This is a moot point. Approximately we may make $\frac{m}{\gamma}$ equal to the molecular volume in the solid state. Chemistry teaches that the volume of solids, even at the absolute zero, is not appreciably different from the volume at ordinary temperature. If the molecular volume in the solid state is not known, we must use that of the liquid state; it makes no difference as regards these calculations.

If we for $O_2$ make $\frac{m}{\gamma} = 25$, we find the diameter = 164 mm.
„ $N_2$ „ = 31, „ „ = 176 mm.
„ $Cl_2$ „ = 42, „ „ = 195 mm.
„ $H_2O$ „ = 18, „ „ = 147 mm.
„ benzene „ = 86, „ „ = 247 mm.
„ alcohol „ = 57, „ „ = 216 mm.

(By kindness of Prof. C. M. Guldberg.)

but the world's wonder of a microscope, which is said to have been exhibited at the World's Fair at Chicago, only magnifies a poor 12,000 times. Besides, if a microscope could be constructed to magnify sufficiently, we should, in order to illuminate the object, require 5,400 times as much light as with our present instruments; and, what is still more serious, the atom which is such a lively being, moving at a speed of half a mile per second, would first have to be killed, which we have yet to learn how to do. Thus there is, I am afraid, no hope of our ever indulging in the sight of an atom or a molecule.

The motions of the vortices or atoms and molecules are increased by addition, and diminished by reduction, of heat. Both motions, peculiar to vortices, are affected in this way; but as it is an essential part of the theory of vortices that they shall remain in motion for ever, they cannot, even if cooled to the absolute zero, come to a complete standstill, and incorporate themselves with the surrounding ether; that would be destruction of matter, all would be ether, and that is incompatible with the principle of conservation of matter. Besides, although we have not been able to produce the temperature of the absolute zero (−273°), and never shall, we have in recent times come pretty close to it, a temperature of −200° having been produced;[1] but no signs of shadowiness were observed: on the contrary, matter in such extreme cold was more palpable than ever. On the other hand, scientists have proved that chemical action entirely ceases even before so low a temperature is reached. Sulphuric acid, for instance, is perfectly indifferent towards sodium hydrate already at −125° (*Compt. Rend.* cxv. p. 814). The form of motion which we call affinity between different molecules seems at that temperature to be wholly extinct, but the other form of motion, the affinity between homogeneous molecules and between the atoms of which they are formed, does not appear to be much impaired by the lowest temperatures we can produce.

These are the physicists' views on the atoms and molecules, represented, of course, in a popular way, without such learned intricacies of the mathematician as are not within the province of the chemist. His researches go less in the direction of what atoms are than in the study of their chemical properties. Therefore he does not lay so much stress upon the form of the atoms themselves, which to him is a minor question, as on the form of the forces of mutual attraction or repulsion in the different sorts of atoms.

We have, with few exceptions, hitherto represented the directions of these forces (affinities or valencies) as lying in the plane of the paper upon which they are represented. Such representation is, however, not probable. The atoms themselves are certainly not minute pancakes with dimensions in the geometrical plane only; they are most likely stereometrical bodies with dimensions in space, and though this view was accepted as probable many years ago, its importance and its consequences were not recognised until fifteen or twenty years ago, but since then it has been furthered to an astonishing point of development.

It is the carbon-atom, almost solely, that has been theorised upon; a little attention has been given to nitrogen, and scarcely any to the rest; but carbon is also the most important of all, and many formerly mystic facts have found their ready explanation by Stereometrical Chemistry, or the Theory of the Position of Atoms in Space.

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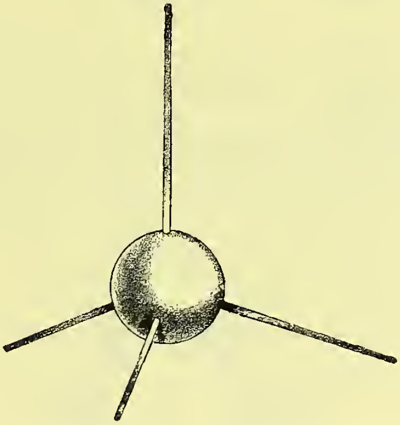
[1] Air was condensed to a liquid at that temperature at the meeting of the Royal Institution, January 20, 1893.

## POSITION OF ATOMS IN SPACE

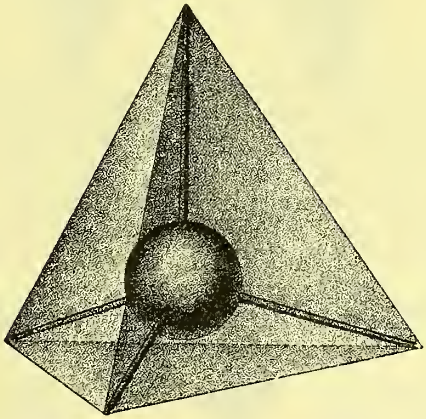
We may suppose that the form of the carbon-atom is spherical, and has its four valencies equidistantly distributed over its surface, from which each is perpendicularly projected into space.

Fig. 1537



If we connect the ends of the valencies by lines we have a regular tetrahedron, in the centre of which lies the carbon-ball, stretching out its valencies to the four vertices of the tetrahedron:

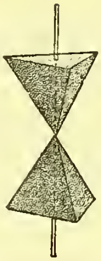
Fig. 1538



Instead of representing the carbon-atom as a ball with four valencies, it will simplify matters to hereafter represent it as a tetrahedron.

If two carbon-atoms unite by single linkage they will do so, of course, through a valency of each. These two valencies joining in a straight line will form a common axis of the two tetrahedrons going through the two united vertices, the centre of each carbon-ball, and the centres of the opposite faces of the two tetrahedrons.

Fig. 1539

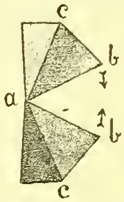


This axis always remains in the straight line of direction if left to itself, and not under the influence of other forces; but has a certain degree of elasticity, and may be bent when the atoms form a double bond or a closed ring.

The atoms, however, move freely round this axis; in fact, they are supposed to oscillate incessantly round it like the balance-wheel in a watch, but immensely quicker. One vertex oscillates opposite to a vertex in the other carbon-atom, the mutual position of the carbon-atoms being determined by the atoms or groups joined to the vertices, so as to bring such groups as have the greatest affinity opposite to each other (*stable compounds*). If they are not in this position (*unstable, labile compounds*) they are inclined to turn round until the stable position has been found. This is greatly facilitated by increasing the oscillations through the application of heat.

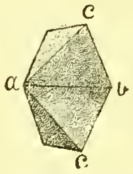
The forming of a double bond is effected by two opposite vertices approaching until actual contact. A triple bond is formed from a double bond by another pair of opposite vertices (*c*) approaching and joining. The following illustrations show the progress and formation of the double and triple bonds between the two above carbon-atoms.

Fig. 1540



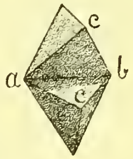
Double bond in process of forming

Fig. 1541



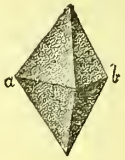
Double bond

Fig. 1542



Triple bond in process of forming from a double bond

Fig. 1543

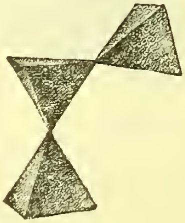


Triple bond

Atoms united by a double bond can oscillate only round the common axis $a:b$; united by a triple bond they cannot, of course, act independently of each other.

If a third carbon-atom joins the two in fig. 1539 it will do so exactly in the same way as the first two united, i.e. by an axis running through one of the vertices and the centre of the respective carbon-balls:

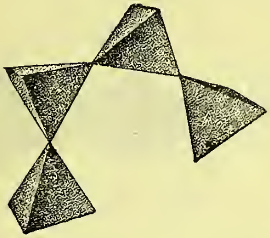
Fig. 1544



Three atoms singly linked

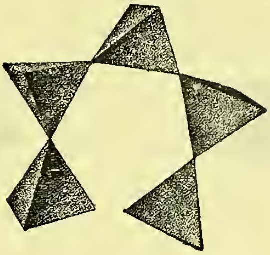
And likewise a fourth and a fifth:

Fig. 1545



Four atoms singly linked

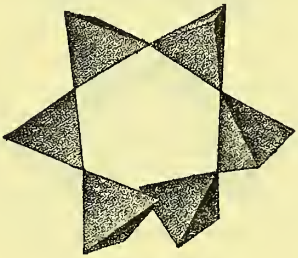
Fig. 1546



Five atoms singly linked

It will be observed that a chain built up in this way, as a matter of course, gradually approaches the ring shape; with the fifth carbon-atom the molecule falls a little short of a complete ring, whereas a sixth carbon-atom would shoot a little past the first carbon in the ring.

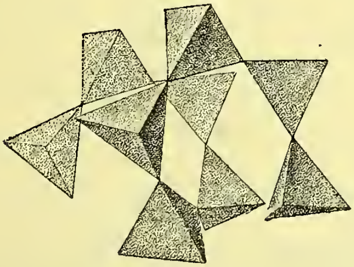
Fig. 1547



Six atoms singly linked

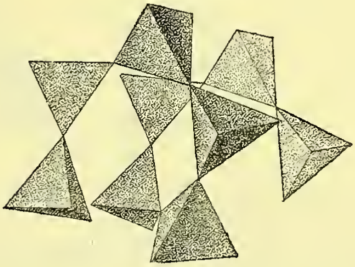
And with six, or still more so with more than six, carbon-atoms, the chain must of necessity assume, according to circumstances, a left or right screw-form—produced, not by any *bending* of the axes, but simply by a *slight turn* of each carbon-atom on its connecting axis.

Fig. 1548



Nine atoms singly linked: left-hand screw-formation

Fig. 1549

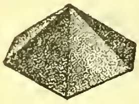


Nine atoms singly linked; right-hand screw-formation

Now we will see what shape a chain with double bonds will assume.

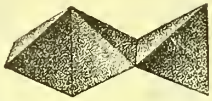
Suppose the chain consists of doubly-linked carbons only, we will gradually lengthen the chain, commencing with two atoms taken from fig. 1541, but laid down on their sides:

Fig. 1550



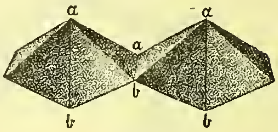
Two atoms doubly linked

Fig. 1551



Three atoms doubly linked

Fig. 1552

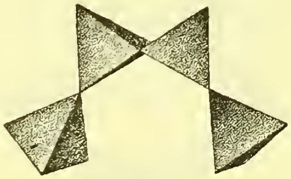


Four atoms doubly linked

Here no attempt at ring-formation is possible; however many carbon-atoms we add to the chain, it will remain a perfectly straight one, the alternate axes round which the atoms oscillate being in perpendicular positions to one another, and excluding any bending propensities.[1]

It is different when there is a combination of double and single linkage. If two carbon-atoms are united by a double bond and two others join, one at each end by a single bond, that is to say, by the point of their vertices, and not in a line by the edges, the structure will appear thus:

Fig. 1553



One double and two single bonds

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[1] A ring-formation, with two double bonds placed as in fig. 1551, has been suggested for some compounds; for instance, sylvestrene (comp. terpenes, p. 50) has been represented by one of the following figures (*Ber.* xxi. p. 172):

Fig. 1552 a

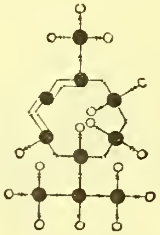
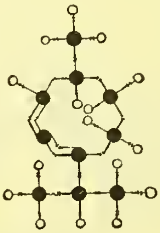


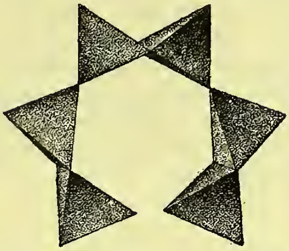
Fig. 1552 b



but this seems quite incompatible with the tetrahedron theory, as an addition of three more carbon-atoms to one of the free valencies of fig. 1551 would have no tendency to meet any of the others, because of the four different directions in which they all point.

A ring-shape is obviously in formation; we will add another carbon at each end by double bonds:

Fig. 1554

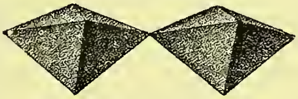


A double and a single bond alternately

Thus we see that six carbon-atoms united in this way are close upon forming a complete ring.

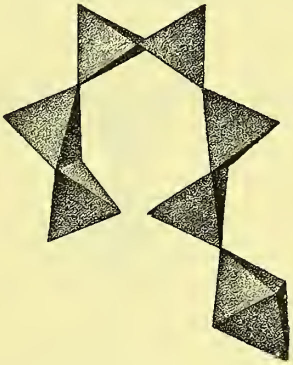
When two carbon-atoms are united by triple bond, only one valency in each is left free to combine with other atoms; therefore anything added must be bound by a single bond. The structure of two such pairs will then be this:

Fig. 1555



They have both one common axis; no matter how many links of the same sort we may put together, the chain will not deviate from the straight line. Even if we construct a chain from a single pair of trebly bound carbon-atoms to begin with, continuing with a structure of single bonds, or mixed single and double bonds, the ring formed will not include the triple bond, because the ring-shape thus formed would be too small to give room for it. Therefore no closed ring is known to contain a triple bond. This sort of linking will be seen from the illustration:

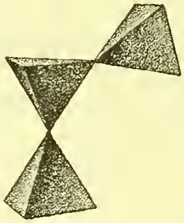
Fig. 1556



It is easy now to understand how and why closed chains are formed, and also the reason for the frequent occurrence of pentagons and hexagons, and why $\gamma$- and $\delta$-hydroxy-acids form lactones, but not $\alpha$- and $\beta$-compounds. The rings are almost ready-made beforehand, and all that is required is a free valency at each end; they will unite through the attracting force between free valencies, and thus complete the ring. When this force is strong enough, it will draw together, though probably with some difficulty, the ends of a bit of chain of three singly linked carbon-atoms, notwithstanding the distance is relatively great; the ring of four such atoms is more easily formed, but the easiest of all are, of course, chains of five or six atoms, because of the ring being all but formed. Even seven will close up, as we have seen with hepta-methylene's derivatives; but from their rare occurrence we may conclude that it is not easily done. The reason for this is probably that the last carbon, with its free valency, is too far away from the other free valency, and its force perhaps lessened by the proximity of the atoms alongside which it runs in screw-fashion. A ring of eight or more successive carbon-atoms seems impossible of formation, though even decagons have been formed by interposing links of other elements, principally nitrogen.

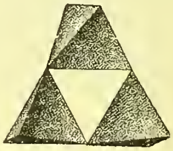
The closing of rings may be thus illustrated:

Fig. 1557



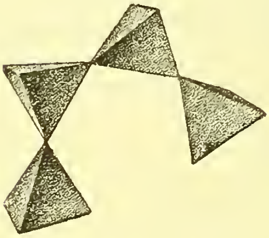
Three singly linked carbon-atoms

Fig. 1557 a



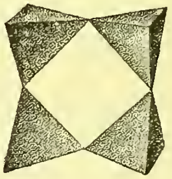
Closing of three singly linked atoms

Fig. 1558



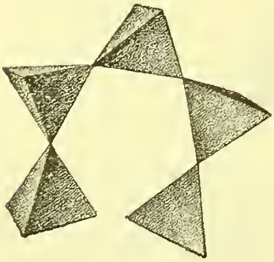
Four singly linked carbon-atoms

Fig. 1558 a



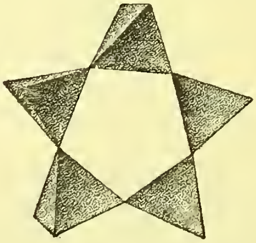
Closing of four singly linked atoms

Fig. 1559



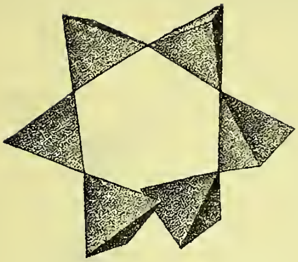
Five singly linked carbon-atoms

Fig. 1559 a



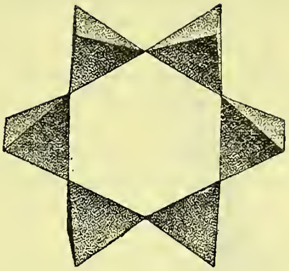
Closing of five singly linked atoms

Fig. 1560



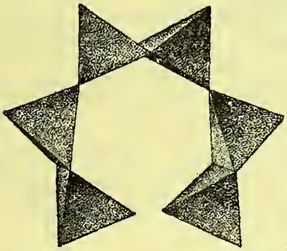
Six singly linked carbon-atoms

Fig. 1560 a



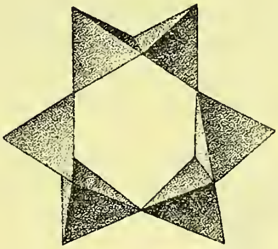
Closing of six singly linked atoms

Fig. 1561



Six alternately singly and doubly linked carbon-atoms

Fig. 1561 a

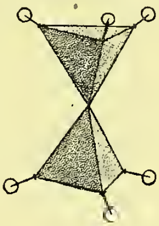


Closing of six alternately singly and doubly linked atoms

We have hitherto made use of carbon-atoms as if their valencies were free, those of course excepted by which they are tied together. We will now see how they behave when all their valencies are engaged in the same, or in different ways.

We will illustrate two carbon-atoms united by single bond, and six hydrogen-atoms attached to their free valencies, using for hydrogens the same signs as before:

Fig. 1562



Ethane

The two carbon-atoms, it will be remembered, are revoluble round their common axis, and can therefore be turned into three different positions, a new vertex each time facing one of the vertices in the other carbon-atom. It will, however, be seen that, in whichever of the three positions we place the two carbon-atoms in the above figure, it makes no difference in the compound regarded as a whole: in all three cases a hydrogen-vertex in one carbon-atom faces a hydrogen-vertex in the other.

We will now introduce a new element to which hydrogen has a very strong affinity, viz. chlorine. The three positions created by turning one of the carbon-atoms round are here represented.

Fig. 1563

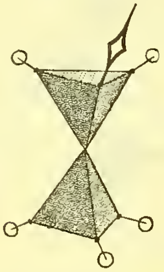


Fig. 1564

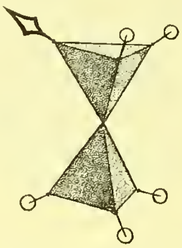
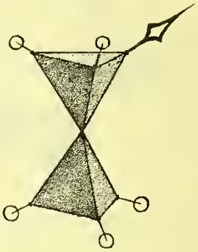


Fig. 1565



Neither in this case do the various positions make any difference; in all of them a chlorine faces a hydrogen-atom, and the other hydrogen-atoms face each other in pairs.

If we now introduce a chlorine-atom in the lower carbon, too, the three possible positions would be these:

Fig. 1566

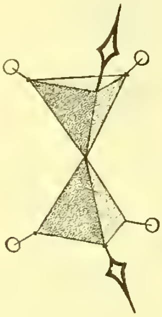


Fig. 1567

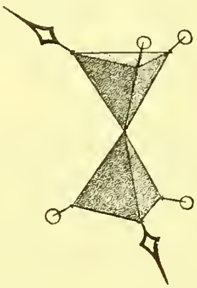
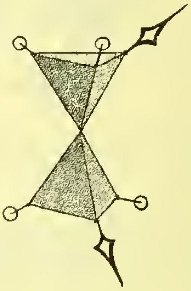


Fig. 1568



In the first figure chlorine has taken possession of a vertex in the lower carbon-atom facing the chlorine in the upper atom. But chlorine has too much affinity to hydrogen to remain there; it will try to get as near one of the hydrogen-atoms as possible, and will therefore move the carbon round its axis until it has arrived opposite a hydrogen. It can do this by turning either to the right or to the left. In the second figure the upper carbon-atom has been turned to the left, in the third to the right. In these positions there is stability. The two figures bear to each other the same relation as a right-hand to a left-hand glove (*enanthiomorphism*), otherwise they are identical, and their chemical properties are exactly the same; in fact, the existence of these two compounds with such difference is solely based upon theory, and supported by no direct fact. In more complicated compounds we shall see the difference indicated by their physical properties.

If the attractive power between the different atoms or groups fixed to one carbon-atom and those placed on the other is not particularly strong, all three positions may be possible; but generally one position seems to be preferred to the others, and is termed the *favoured position*, in which the compound shows itself more stable than in the others, and into which it arranges itself at the first opportunity.

It will now be understood what perhaps has been rather puzzling to the reader, that it is of no consequence in what order the atoms or groups are placed upon the same carbon-atom (*vide* p. 8), provided no favoured position comes into play. They do not, in point of fact, leave their positions; it is the carbon-atom that turns round upon its axis. Further, we can now better understand also the nature of double and triple bonds. The common axis between two carbon-atoms is supposed to possess a certain degree of elasticity, like a steel spring; in order to bend two atoms so that two opposite vertices come in actual contact (*vide* fig. 1539 &c., p. 454) some force is required that will overcome the spring-resistance of the axis. In the earlier part of this treatise we have freely spoken of the removal of two hydrogen-atoms as if it were the easiest thing in the world. That is, however, theory only; we cannot go about picking hydrogens like we do apples and pears from our fruit-trees; in chemical practice we have to resort to devices and to the use of two forces, either affinity or heat, both being most probably but two forms of the same force, motion. We use affinity by placing, on two opposite vertices, bodies that have a great liking for each other, *e.g.* chlorine and hydrogen (as in figs. 1563, 1564, and 1565), which together form hydrochloric acid. If we then approach a new body which has a great affinity to hydrochloric acid, *e.g.* an alkali, that force is so strong as to overcome the elastic resistance of the axis, and make the two carbon-atoms bend towards each other until chlorine and hydrogen come into actual contact and can form hydrochloric acid; but at the same time the vertices of the carbon-atoms also come in contact, and, being left by their chlorine- and hydrogen-appendages, the two free valencies have sufficient affinity to resist the tendency of the elastic axis to raise itself again. There is thus a certain degree of tension in the situation, and on very slight provocation—the approach of two chlorine-atoms, for instance—the connection between the two vertices will snap, and the two carbon-atoms spring back into their original upright position. Therefore double bonds cannot be so strong as single bonds.

If two chlorine-atoms are affixed to the vertices (as shown in fig. 1567 or 1568), it is evident that two faces and not only two edges of the carbon-atoms may close up, and the triple bond be formed.

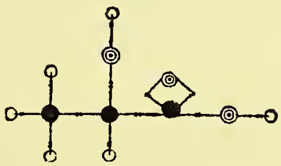
As heat is but another form of motion, it might perhaps at a first glance seem improbable that a less powerful binding should be effected by such means. Still, we know that double and triple bonds are frequently formed through the application of heat. Our theory readily explains that.

The atoms are not supposed to be in a state of static rest in their mutual positions, as frequently mentioned; on the contrary, they are oscillating round the connecting axis. When heat is applied, these oscillations become more and more impetuous, and, as a consequence of the centrifugal force, the path of the upper carbon's vibrations will become more and more depressed, whilst that of the lower carbon will rise, as when a ball fastened to a string is whirled round. At last the oscillation-path of the two carbon-atoms will become identical; that is to say, two of their edges will come into contact, and through their affinity the force by which any appendages are held by the vertices is lessened so much that these appendages are flung off and the double bond established, after which the oscillations take place round the axis $a:b$ (fig. 1541, p. 454). By increased application of heat these oscillations become in turn also so violent that at last the vertices $c:c$ meet, and the triple bond is formed.

With this theory as the base, stereo-isomerism, which we have had occasion to observe so many times, may be easily explained.

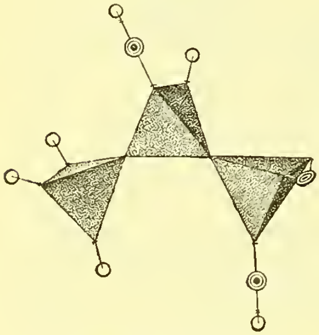
We will as a first example take ethylidene lactic acid, which has been found to exist in three optically different forms. It is composed of three carbon-atoms, one of them having three hydrogen-atoms attached, another a hydroxyl and a hydrogen, and the third is carboxyl. Our usual representation of the compound is this (*vide* fig. 692, p. 179):

Fig. 1569



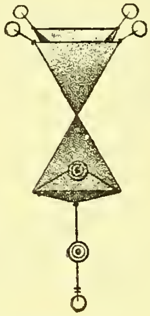
Represented by the stereometrical tetrahedrons, the compound may be illustrated by fig. 1570. It will be noticed that the intermediate carbon-atom has, at one of the top vertices, a hydrogen-atom attached, and at the other a hydroxyl. The mass of the latter is greater than that of the former, wherefore the carbon-atom by the oscillations is thrown slightly out of equilibrium,[1] which will be better observed if we look at it from the side, as shown by figs. 1572, 1573.

Fig. 1570



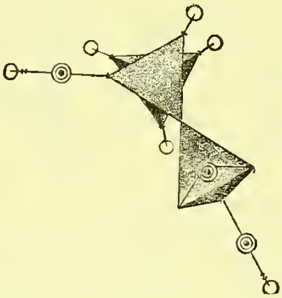
Ethylidene-lactic acid

Fig. 1571



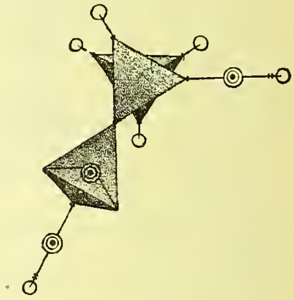
Propionic acid

Fig. 1572



Active ethylidene-lactic acid ; dextro-rotatory

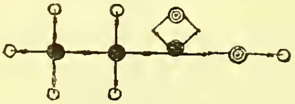
Fig. 1573



Lævo-lactic acid ; lævo-rotatory

The figure 1571 is propionic acid, which we have before (fig. 669, p. 176) represented thus:

Fig. 1574



The intermediate carbon-atom in this compound has a hydrogen-atom on each side, is therefore evenly balanced, and its structure forming part of a ring will cause the molecule to dart through the ether without any rotative movement.

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[1] I am not prepared to prove this assertion, because—even if nothing else were amiss—our imperfect knowledge of the real nature of the force we call affinity makes it impossible to argue the point mathematically. The facts, however, which I am going to submit in the following pages agree so well with the assertion as to make its correctness, in my opinion, highly probable, further supported, as I think it is, by the following considerations : I am unable to find that any optically active compound has been discovered in which the asymmetrical carbon forms an end-link of the chain ; thus no active compound with either one or two carbon-atoms has hitherto been found amongst methane- and ethane-derivatives, though such compounds with an asymmetrical carbon, of course as end-link, do exist, *e.g.* chloro-brom-acetic acid (*Beilst*, i. p. 452 ; *R. & S.* i. p. 544). Activity is found in derivatives of the higher homologues only, commencing with propane, and in these the asymmetrical carbon-atom is always—as far as they have been investigated—an intermediate one bound on two or more sides by other carbon-atoms, never an end-link. Now, the oscillations of an intermediate carbon atom must evidently be different from those of an end-carbon, because the latter are formed from one motion only, while the former must be the resultant motion of two or more oscillations which such a carbon-atom performs in harmony with those of the carbon-atoms to which it is joined, being kept by the force or forces (which in the absence of a more definite knowledge of their nature I will call the centrifugal force) in a distinct position dependent on such factors as centres of gravity or inertia, moments of inertia or forces, &c. ; it is impossible at present to formulate the law according to which these factors would act, but probably it will be to the effect that 'atoms are formed into groups in which the moment of inertia round the axis of rotation is the smallest possible,' or something like it. When those factors are altered from a centric to an eccentric influence, as they are by the unequal loading of an asymmetrical carbon, the connecting axes would—if the side-carbons remained in their positions—be subjected to a strain, which, if not entirely removed, must, at least, be considerably lessened by the asymmetrical carbon turning round on one of the axes and carrying the other carbon-atom with it into the new position ; an arrangement that it consequently prefers, as asserted above. The oscillations and their influence upon atoms and molecules are still enveloped in mystery, and we should not be surprised to learn some day that they are to the molecules what the movements of *cilia* are to the lower animals—their propelling force. All this belongs to the future chemistry, the kinetic theories, into which I shall not, for excellent reasons of my own, go any further.

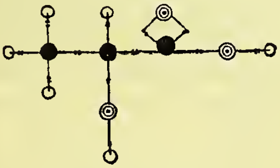
But when a hydroxyl, instead of one of the hydrogen-atoms, is planted upon this carbon-atom, the balance is disturbed, and the carbon-atom thrown over to one side by the centrifugal force of the oscillating movement. It can do this by a turn on *one of the axes* by which it is connected with the two other carbons; but in doing so it will have to carry with it the carbon-atom to which it is bound by *the other axis*, transforming thereby the ring form into that of a screw, and the molecule, now rushing through the ether, must assume a rotatory motion. The form of the screw will depend upon the side to which the hydroxyl is attached; fig. 1572 represents a right-hand screw, which, revolving many hundred thousand times per second, will throw the plane of the polarised light that enters one end of the screw over to the left hand of the spectator at the other end. In the same manner the light will be thrown over to the right from the structure (fig. 1573), which forms part of a worm of a left-hand screw.

If these two structures be present in equal numbers, the light will be thrown just as much to the right as to the left; in other words, there would be no deviation of its propagation from the original plane. Such compounds are termed inactive isomers.

It will be noticed that the two carbon-atoms on each side of the intermediate one are differently engaged, one being a methyl ($CH_3$), the other a carboxyl ($CHO_2$). The intermediate carbon-atom is thus differently engaged on all four valencies by (1) a hydrogen-atom, (2) a hydroxyl, (3) a methyl, and (4) a carboxyl. It is therefore termed an *asymmetrical carbon-atom*, and in all compounds which cause the rotation of light, such an asymmetrical carbon-atom is said to be always present (though I doubt the correctness of this assertion, *vide* p. 467 *seq.*). The essential thing is not the two side attachments only: in the above case the hydrogen and the hydroxyl, though the difference in their mass (and perhaps also in their interatomic distance[1]) is no doubt primus motor; but a difference in the combinations of the two other valencies is just as necessary, because, being of unequal mass, the one with the greatest would probably remain stationary, and the one with least mass would be carried into a new slanting position with the asymmetrical carbon-atom,[2] whereas when of equal mass both would change position simultaneously with the asymmetrical carbon, and therefore the relative position of all three would undergo no change.

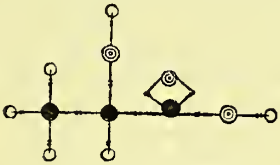
With the symbols adopted in the foregoing part for representing structures pictorially, the optical differences of the two lactic acids might have been indicated in this way:

Fig. 1575



Dextro-lactic acid

Fig. 1576



Lævo-lactic acid

But, as explained before, comparability and conspicuity would suffer, and therefore, apart from the fact that the exact position of the hydroxyl is known in comparatively few compounds, this distinction has been omitted, except in one or two cases; for instance, in some structures of the sugars.

When two asymmetrical carbon-atoms are present in a compound, four different isomers are admitted by the theory, and facts have confirmed the theory.

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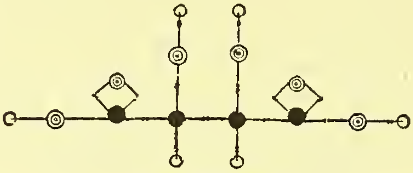
[1] *Vide* Guye, *Étude sur la dissymétrie moléculaire*, Génève, 1891.

[2] In the figures I have let the carboxyl-group follow the movement of the asymmetrical carbon, and left the methyl stationary instead of reversing the process. This has been done on account of the difficulty of representing the correct position in drawing without leaving out of sight essential points that would be hidden behind the atoms nearer to view.

Such a compound with two asymmetrical carbon-atoms is tartaric acid, represented by our system (fig. 731, p. 187) thus:

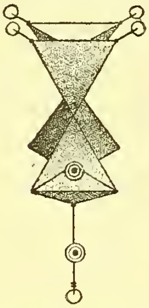
Fig. 1577



Tartaric acid

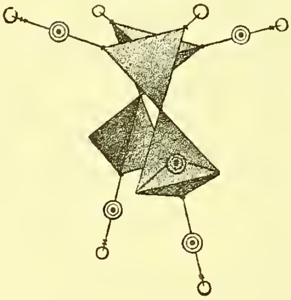
Represented by tetrahedrons, and seen from the same point of view as the lactic acids just mentioned, the different isomers may be illustrated in this way:

Fig. 1578



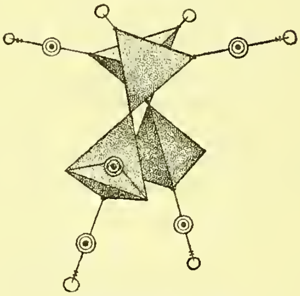
Succinic acid
(*vide* fig. 714, p. 185)

Fig. 1579



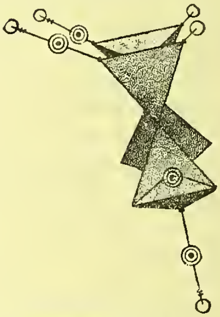
Dextro-tartaric acid

Fig. 1580



Lævo-tartaric acid

Fig. 1581

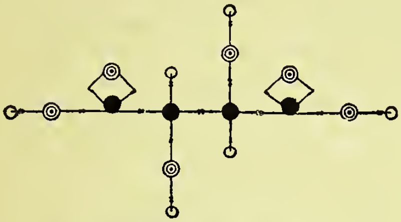


Meso-tartaric acid

The first of these figures is succinic acid, from which the different tartaric acids are formed by substituting hydroxyls for the two top carbon-atoms' hydrogens. It will be seen that these two carbon-atoms in succinic acid are in a state of equilibrium, being evenly loaded on both sides with hydrogens; but if we, on each of them, replace a hydrogen by hydroxyl, as in fig. 1579, the two front carbons will incline to the left, and the two rear carbons to the right, evidently forming part of a right-hand screw, which, darting through the ether, will probably assume a rotatory motion, and undoubtedly influence the plane of the polarised light passing through it, giving it a turn to the left of the observer. In fig. 1580 the positions are reversed; consequently the molecule will assume the form of a left-hand screw, throwing the light over to the right. In fig. 1581 both hydroxyls have taken up positions on the same side of the molecule; consequently both pairs of carbon-atoms are thrown over to the same side; their positions relative to each other are not altered; they remain the same as in succinic acid, forming a ring and not a screw; the molecules rush about without any rotatory motion, and the polarised rays pass unaffected through them, i.e. it is an inactive form of isomerism. This figure may also be regarded as composed of the two front carbons of fig. 1579 and the two rear carbons of fig. 1580, and is, therefore, generally described as consisting of half a molecule of dextro- and half of lævo-tartaric acid; but, of course, it is succinic acid in which the hydroxyls have replaced hydrogens on the same side of the molecule.

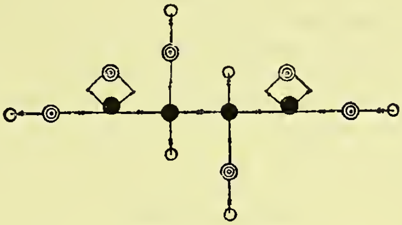
Another inactive tartaric acid, the fourth isomer, is a mixture of equal parts of *whole* molecules of dextro- and lævo-tartaric acids, and termed racemic acid, as mentioned, p. 188. Such mixture can by crystallisation be mechanically separated into its components, the crystals of one acid being the reflected image of the other—exactly like the two molecules, figs. 1579 and 1580, which is not the case with the inactive form represented by fig. 1581. Illustrated by our pictorial symbols, the different isomers of tartaric acid might—more correctly than on p. 187—be represented thus:

Fig. 1582



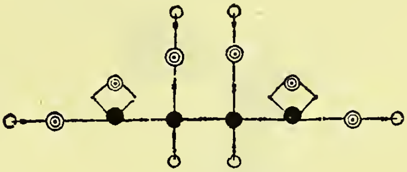
Dextro-tartaric acid

Fig. 1583



Lævo-tartaric acid

Fig. 1584

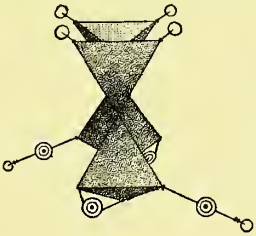


Meso-tartaric acid

It should be stated here that the above explanation of optical activity has not received the sanction of authorities—at least not yet—for the reason, amongst others, perhaps, that the theory has not been propounded before, that I am aware of;[1] I may therefore be allowed to support the idea by some more reasons for its probability, though not a proper subject for the purpose of this treatise.

Before proceeding, however, it is necessary to explain that the figure (1578) of succinic acid is under no circumstance quite correct, because it represents an unstable structure of the molecule, the two carboxyl-hydroxyls (one is behind the foremost carboxyl, and therefore not visible) being in close proximity, although under the attraction of hydrogens near by. It represents, however, the position of the atoms at the moment of the acid's formation into anhydride; a more correct representation would be

Fig. 1585



because here the hydroxyls would be facing hydrogens, besides being themselves farther apart, and thereby creating stability in the structure. But this position of the hydroxyls would greatly impair the lucidity of the other figures, even if in the formation of tartaric acid from succinic acid they stuck to their places, which they do not do, because the carboxyl must turn round its axis to find a stable position, according to which side of the molecule the alcoholic hydroxyls are affixed to. I have therefore preferred giving the carboxyls the unstable, but more neutral position; the more so as it is not of consequence to the further development of the theory. But even with such corrections the structure given above to succinic acid is not an interpretation of the views of our greatest authorities on this subject (*Wislicenus Raümliche Anordnung der Atome*, Leipzig, 1889). I have deemed it sufficient for the stability of the structure to make the carboxyl's hydroxyls each face a hydrogen, at the same time removing them from each other by turning the carbon-atom round its axis; but according to the said authorities the proximity of the carboxyls themselves, *in their entirety*, causes the instability of the structure, and, in order to avoid this proximity, one of *the two carbon-atoms to which the carboxyls are affixed* makes a turn round *their* common axis, carrying with it the carboxyl, and placing it in the position represented in the following figure:

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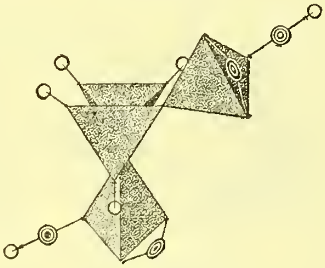
[1] The theory is strictly a physical, and further, development of Guye's mathematical deductions (*l.c.* p. 463) with which it is in perfect accord.

Fig. 1586



Succinic acid

If this be the correct structure then succinic acid has already the screw-form, and the theory advanced above must be abandoned, whether we assume that the unequal loading of the two intermediate carbon-atoms by hydroxyls influences their mutual positions or not. In the latter case all the structures, whether optically active or not, will have screw-formation; in the former case the structures will have to be represented thus:

Fig. 1587

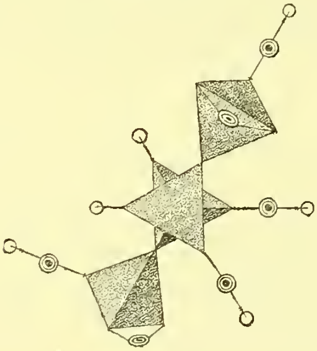
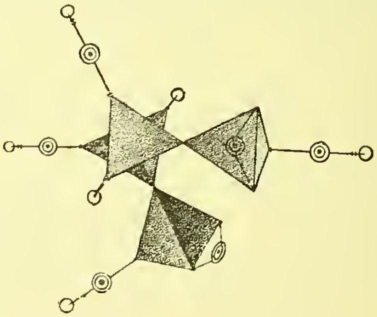


Fig. 1588

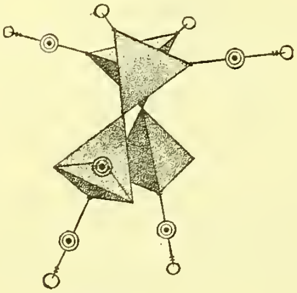


The angle to which the two atom-complexes will be inclined by the weight, or mass, of the hydroxyls cannot exceed that given in the figures without endangering the stability of the structure by the mutual approach of two hydroxyls; indeed, this very danger was the reason why the structure of succinic acid in fig. 1586 was adopted. We may therefore assume that the above representations are correct, provided the structure of succinic acid (fig. 1586) is correct, and we see then that one of the optically active tartaric acids has decidedly no screw-formation. Of course, it would, therefore, be fatal to the dependence of optical activity on screw-formation if fig. 1586 were a correct representation of the structure of succinic acid; but I do not see the necessity of accepting it as such: it seems to me not even probable. There is no reason for assuming the existence of any repelling force between the two carboxyls that should necessitate such extreme measures as turning round a whole complex of two carbon-atoms; on the contrary, they are always very willing to unite by dropping a molecule of water when the necessary energy is provided; on the other hand, the electro-positive hydrogen has attractions after which the electro-negative hydroxyl is always running. In fig. 1578 the two hydroxyls (one of which is hidden behind the front carbon) are in a position in which they have to choose what to do; either combine, dropping a molecule of water, or turn the carbon-atom a little round its axis in order to take up the position opposite one of the hydrogens; they choose the latter expedient for several reasons; partly because the formation of water requires more energy than they are possessed of, whereas, probably, none is required for turning the carbon-atom; partly because the attraction between hydroxyl and hydrogen, under the circumstances, is greater than between the two hydroxyls; and finally, because the law of preservation, perhaps, exists for a molecule's structure as well as for matter generally, wherefore it prefers an arrangement in which its structure is as little disturbed as possible. It is natural that it should choose an arrangement by which the greatest stability is insured, and therefore the two hydroxyls go one to the right and the other to the left, as indicated in fig. 1585, instead of both to the same side, by which the instability on account of the proximity of the hydroxyls would continue to exist, only in a lesser degree. For these reasons I feel inclined to consider the structure of succinic acid more correctly represented by fig. 1585 than by fig. 1586, and the screw-theory unimpeachable from that side. At first sight it may perhaps be objected to the theory that the effect of the rotatory movement of the molecules upon the plane of polarised light will be neutralised by the fact that they move forwards and backwards, and that the number of one sort must equal that of the other; it should, however, be remembered that the light is also moving and only in one direction; consequently it would transverse many more of one sort by meeting those returning than of the other, by overtaking those travelling the same way as the rays. In order to carry the theory out also in closed chains with an asymmetrical carbon-atom in the ring, it becomes necessary to assume a certain degree of elasticity in the bonds connecting the carbon-atoms, sufficient for a screw-like formation of the ring; when we see how much the chemical properties of compounds are alike, if their only structural difference is a breakage of the closed chain, the assumption of such an elasticity seems justifiable, as exemplified further on (*vide* fig. 1588 E).

Since Pasteur, in the year 1848, separated racemic acid into dextro- and lævo-tartaric acids, and amongst other possible causes of their optical differences suggested, in a general way, a screw-formed arrangement of the molecules, several other scientists have tried to solve the difficulty in different ways, some of them utilising Pasteur's idea. These attempts at explaining the optical properties, though in most cases very ingenious, do not seem to have gained general approval, perhaps just because they have been too ingenious, and science, for want of an acceptable explanation or theory, has had to content itself with the following postulate dating from stereo-chemistry's earliest days: *Every active compound has an asymmetrical carbon-atom, but not every compound with an asymmetrical carbon-atom is optically active.* The latter part of the postulate has since then been questioned, because chemists have in a great many cases succeeded in separating such compounds as were formerly considered inactive, mostly in the same way as Pasteur produced the components of racemic acid through the activity of living organisms (*Penicillum glaucum*). This success has caused many chemists to abandon the latter part of the postulate, and to prognosticate the separation of all compounds with an asymmetrical carbon-atom into two compounds with opposite optical properties, even such as consist of the asymmetrical carbon-atom only, *e.g.* chloro-bromo-iodo-methane, CHClBrI (*Stereochemie von Dr. C. A. Bischoff*, 1893).

The above rule applies only to compounds in which but one asymmetrical carbon-atom is present; when there are more the rule is modified, the modifications being almost as numerous as the contingencies; but even thus, difficulties are met with which have not been explained away in a satisfactory manner; for instance, asparagine (fig. 1179, p. 329) is a compound with only one asymmetrical carbon-atom, and we are prepared to find, in analogy to the lactic acids, three optically different asparagines; three have actually been found, two active and one inactive; and it should consequently be possible to prepare the latter by mixing the two former in equal quantities; but in point of fact it cannot be produced in this way (*Ber.* xix. p. 1694), and a structure different from that of the active form has therefore been suggested (fig. 1179, A and B, p. 329), without, however, supplying an explanation of its inactivity. Further there are compounds without any asymmetrical carbon-atom, *e.g.* some terpenes and glycerides, which undoubtedly are possessed of optical activity; a fact of which no explanation has been attempted—I have not found the latter even mentioned in treatises on the dependence of optical activity on an asymmetrical carbon. Again, there are active compounds whose derivatives are less active, sometimes indeed inactive, or even with reversed activity, all of which we have to accept as facts for which the asymmetrical carbon offers no explanation. The screw-theory, it seems to me, explains these anomalies in an extremely simple, natural, and unconstrained way. The asymmetrical carbon, which in the postulate is all important, plays in this theory but a secondary part, and is only of moment as the agent through which a molecule is caused to assume a screw-form; everything depends on the screw-form, and the form of the screw depends upon the radicals attached to the carbon-atoms, what they are and where they are attached. We will take tartaric acid as an example. We have seen that it is composed of four carbon-atoms, two of which constitute asymmetrical carbons, and the other two carboxyls. Let us, for the sake of brevity, call the side-appendages to the former, wings, and the latter the tails. In this case one of the wings in each pair is hydroxyl, and the two carbon systems, of which tartaric acid consists, is thereby caused to incline in different directions, the two forming an angle, determining the pitch of the screw, and through it the rate of velocity with which it will rotate. If, instead of hydroxyls, the *wings* are represented by radicals of greater mass, the angle, or in other words the pitch, will be increased; and, assuming that the speed with which a molecule travels is not thereby sensibly affected, its rotation will decrease in proportion as its pitch increases. If additions to the mass of such radicals are constantly made, a point will soon be reached when the helix is stretched out to a straight line, the molecule losing the form of a screw; by continued additions a screw of the reversed worm will begin to form, with constantly decreasing pitch and increasing speed of revolutions. If, on the other hand, we increase the mass of the *tail* by similar appendages, the angle between the two carbon systems will be reduced, the pitch decreased, and the rotation increased. Thus, by adding either to the wings or to the tail, or to both, the movements of a molecule and its consequent power of turning the polarised plane can be regulated at will, increased, decreased, stopped, or reversed. The action is well illustrated by a piece of cord: if while kept taut it is untwisted the strands will form straight lines, and continued motion will twist them, in screw-form, in the opposite direction to that they previously had. The diagrams explain it easily:

FIG. 1588 A



Tartaric acid

FIG. 1588 B

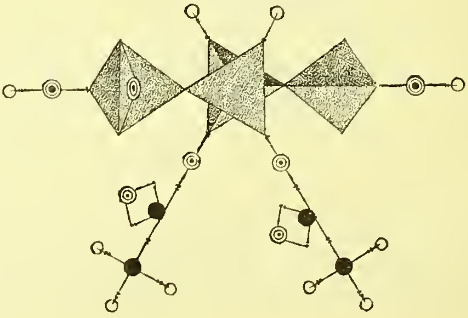
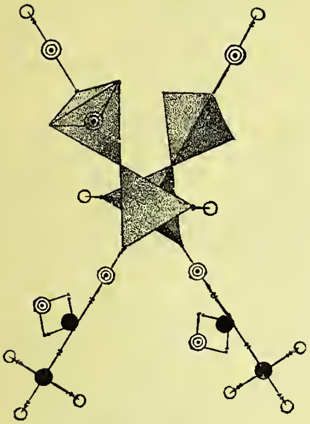
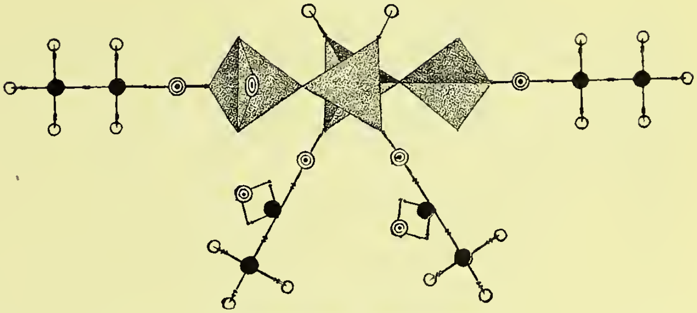


Fig. 1588 c



Di-acetyl-tartaric acid

Fig. 1588 d



Di-acetyl-tartaric-ethyl-ether

Fig. 1588 A is tartaric acid, from which we form di-acetyl-tartaric acid by substituting acetyls for the alcoholic hydroxyls, representing the *wings* of the two carbon systems, the divergency of which is consequently so much increased that the helix of the original positive screw-form is not only stretched out into a straight line (inactivity), as represented in fig. 1588 B, but has passed into the reversed negative screw-form seen in fig. 1588 C.

If we now attach radicals to the *tails* (carboxyls) of di-acetyl-tartaric acid the effect of the wings will be counteracted, and a re-formation into the original positive screw commenced; thus, if di-acetyl-tartaric acid is converted into its compound ether by attaching methyl to the tail, the negative turning power of the compound is considerably lessened, yet still negative; but if ethyl-ether is formed the structure will be nearly that represented by fig. 1588 D; that is to say, the helix will have just passed the straight line (inactive form) and formed a positive screw of very high pitch and small turning power. If iso-butyl is employed as substitute in the tail the effect of the acetyl substitution in the wings is almost counterbalanced, the di-acetyl-tartaric iso-butyl-ether having nearly the same optical activity as tartaric acid itself.

If, instead of acetyl in di-acetyl-tartaric acid, we employ, *as wings*, a radical of still greater mass, *e.g.* benzoyl, the effect is further increased, the di-benzoyl-tartaric acid turning the polarised light far more to the left than the corresponding acetyl compound. Again, if we leave the wings of tartaric acid undisturbed, and make additions to the *tails* only, the pitch of the screw is decreased, the rotation and consequent power of turning the polarised plane are increased, according to the mass of such additions. The following tables, taken from *Stereochemie nach J. H. Van 't Hoff's Dix Années dans l'histoire d'une théorie bearbeitet von Dr. W. Meyerhoffer*, 1892, seem to strengthen the screw-theory:

| | αD at 20° |
|---|---|
| Tartaric methyl-ether | + 2·14 |
| ,, ethyl- ,, | + 7·16 |
| ,, propyl- ,, | + 12·44 |
| ,, iso-butyl-,, | + 19·87 |
| Di-acetyl-tartaric acid | — 23·14 |
| ,, ,, methyl-ether | — 14·29 |
| ,, ,, ethyl- ,, | + 1·02 |
| ,, ,, propyl- ,, | + 6·52 |
| ,, ,, iso-butyl-,, | + 10·29 |

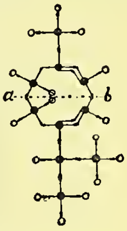
| | |
|---|---|
| Di-benzoyl-tartaric acid | –117·68 |
| ,, ,, methyl-ether | – 88·78 |
| ,, ,, ethyl- ,, | – 60·02 |
| ,, ,, iso-butyl-,, | – 41·95 |

Just as easily may the optical behaviour of asparagine be explained. Here, only one asymmetrical carbon is present, the wings of which are the same, H and $NH_2$, in both the active and inactive forms (*vide* figs. 1179, A and B, p. 329); but the tails are essentially different. In the active form, fig. 1179 A, the heavier tail ($CH_2CONH_2$, atomic weight $=58$) is to the right of the asymmetrical carbon, the lighter tail ($COOH=45$) is to the left. In the inactive form the heavier tail ($CH_2COOH=59$) is to the left, the lighter ($CONH_2=44$) to the right; consequently the left one will in the active form follow the inclining movement of the asymmetrical carbon, while in the inactive form it would under ordinary circumstances be the right tail. The circumstances are, however, not ordinary in the case of asparagine; the stationary tail of inactive asparagine consists of the carboxylic radical of acetic acid, a strongly electro-negative body, whilst the movable tail finishes in an amido-group, a strongly electro-positive body, the negative effect of the neighbouring carbonyl being neutralised by the amido-group of the asymmetrical carbon. In the stereometrical configuration the two tails come into close proximity, and their affinity will resist the effort of the asymmetrical carbon to separate them; the molecule will consequently retain its ring-form without any rotatory property. In the active form of asparagine the arrangement of the electro-positive and negative groups is entirely altered; the asymmetrical carbon has here gone over to the carboxyl tail, the positive amido-group almost neutralising the negative character of the now movable left tail, whilst the basic property of the other, now stationary, right tail is greatly impaired by the neighbouring carbonyl, which is no longer influenced by the proximity of the asymmetrical carbon's amido-group. The affinity between the two tails is therefore not sufficient to resist the effect of the unevenly balanced asymmetrical carbon, and the molecule will assume the screw-form, and with it optical activity. In asparagine the screw-formation was prevented by the force binding the two tails together, but we have instances of optical inactivity that may be explained by the same force preventing the inclining movement of the asymmetrical carbon by binding the wings together. Thus some diversity of opinion has reigned as to the influence which substitution of halogens for hydroxyls exercises upon certain compounds. Some chemists have obtained from malic acid an active, others an inactive, form of mono-chloro-succinic acid (*Ber.* xxvi. p. 210). If we look at succinic acid, fig. 1578, p. 464, or malic acid, fig. 1591, p. 469, we shall see that a chlorine atom, substituting one of the hydrogen wings of the former or the (alcoholic) hydroxyl wing of the latter, will face a hydrogen representing an opposite wing. The two may have sufficient affinity to resist the force that would otherwise throw them out of balance, and the molecule will become inactive; but if through another mode of preparation—for instance, in a higher temperature—the chlorine atom is moved away from the hydrogen's sphere of action the centrifugal force comes into full play upon the unevenly balanced carbon-atom, and will sustain the molecule in the resulting screw-form and consequent activity.

It follows from this theory, as a matter of course, that difference in atomic weights of the groups round an asymmetrical carbon is not absolutely necessary for optical activity; in the case of equality all depends upon the configuration; a group whose mass is spread out in an elongated form will affect the movements of a molecule in a way other than when the mass is concentrated round a point. In fact, Guye has experimentally proved that, *e.g.* ethyl, $C_2H_5=29$, and formyl, $COH=29$, are consistent with optical activity.

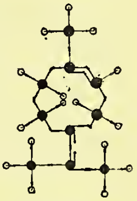
Optical inactivity of compounds without any asymmetrical carbon-atom has been an article of belief considered so incontestable that structures have had to conform themselves to the theory, not the theory to structure. A. v. Baeyer has, however, recently (*Ber.* xxvii. p. 450) with irrefutable stringency proved that, unless the whole tetrahedron-theory is mere fiction, di-pentene (*vide* terpenes, p. 50) cannot have any asymmetrical carbon-atom in its structure; but di-pentene is simply a mixture of the two active compounds, dextro- and lævo-limonene; neither, therefore, can the latter have such a carbon-atom in *their* structures. One such case is sufficient to shake the asymmetrical postulate to its very foundation and make us look for something nearer the truth. The screw-theory seems to me capable of taking up the mission. An atom has admittedly a sphere of action, or, in other words, there must be a certain elasticity in the force binding one atom to another so that they can, to a certain extent, be removed from each other without the bond breaking. When we now look at the structure of di-pentene as demonstrated by A. v. Baeyer we see the line *a b* dividing it into halves, and if the elasticity of the bond at *a* allows the lower half to turn horizontally to the right or left on the point of contact between the bonds at *b*, a right- or left-hand screw is evidently formed, and with it are the necessary requirements for optical activity created. It now only remains to see if a plausible cause can be adduced explaining a strain upon the bond *a*, sufficient to make one of the halves turn on the pivot at *b*. I think the unsymmetrical configuration of the iso-propyl-group, in conjunction with its greater mass as compared to the methyl on the top-half of the molecule, quite sufficiently accounts for the formation of a screw when we remember that according to the tetrahedron theory the position of two of iso-propyl's carbon-atoms must be outside the plane of the hexagon, and must be kept there by the oscillating movements of the atoms; a position that has not found a true representation in the above illustration. This view receives some support in the fact that optical activity ceases when the double bond $\Delta^3$ shifts to $\Delta^{4(8)}$ (comp. p. 50), that is to say, when di-pentene is converted into terpinolene (fig. 1588 F), the structure of which A. v. Baeyer has determined with the same exactitude as that of di-pentene; on account of the double bond by which the iso-propyl group is now bound to the hexagon, the formerly unsymmetrical position of its two carbon-atoms are, in accordance with the tetrahedron-theory, converted into perfectly symmetrical positions in the plane of the hexagon, as represented in the figure.

Fig. 1588 E



Di-pentene

Fig. 1588 F



Terpinolene

The optical activity of compounds consisting of a long chain without any asymmetrical carbon has been very little inquired into. According to the screw-theory all compounds of more than five or six such carbon atoms assume by necessity the screw-form (*vide* figs. 1548 and 1549, p. 455), unless they assume a possible, but perhaps not probable, zig-zag form; some glycerides have been found optically active, but only further investigations can confirm or contradict the theory.

The theory is so full of consequences that its invalidity if quite incorrect must soon manifest itself, though it may perhaps take a long time to make it acceptable if it be a step in the right direction. I shall only, as an example, mention one or two of these consequences.

We have seen that tartaric acid is composed of two exactly similar groups, and that therefore an inactive acid is produced by placing both hydroxyls on the same side of the molecule, no matter whether on the right or left side; but there are many compounds in which the two groups are not similar; if the hydroxyls are placed on the same side of such compounds the two groups will incline, but not to the same degree, the one with a lighter tail inclining more than that with a heavier. Also in such case the structure represents a screw, but with a smaller pitch, and consequently optically more active than when the hydroxyls are placed on each side of the molecule. Two sorts of such screws with smaller pitch may, according to the theory, be formed—one as a right- the other as a left-hand screw, besides the two in which the hydroxyls are placed on different sides of the molecule.

Where screw-formation is impossible, optical activity is excluded; an asymmetrical carbon-atom that has not on two opposite sides other carbon-atoms cannot form a screw, therefore an inactive compound like chloro-bromo-iodo-methane (hypothetical?), mentioned p. 467, will always remain inactive, and cannot be split into two compounds with optically opposite properties, as asserted by the asymmetrical carbon postulate; nor can compounds like ethyl- or propyl-nitrolic acid (*vide* fig. 1085, p. 305) ever turn active, in spite of their asymmetrical carbon (provided, of course, the structure is correct as there represented, and supposing nitrogen does not possess the same capability of forming screws as carbon), because they have not this qualification necessary for screw-formation.

The screw-theory, if correct, may also assist us to a more exact knowledge of the arrangement of groups round an asymmetrical carbon. The structure of active amyl-alcohol, for instance, may be illustrated in three different ways, according as it pleases us to arrange the various groups.

Fig. 1588 G

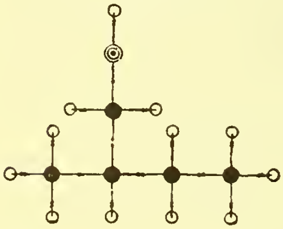


Fig. 1588 H

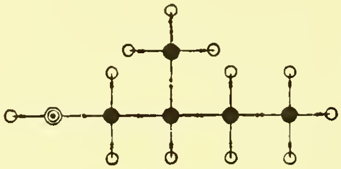
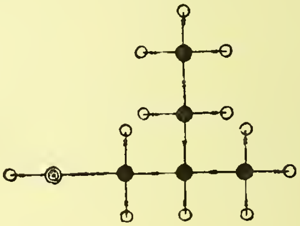


Fig. 1588 I



But, of course, only one of them can represent the actual structure. Now, we know that lævo-amyl-alcohol turns the polarised light a little to the left $(\alpha\,\mathrm{D} = -5{\cdot}7)$; but if we replace the hydroxyl by chlorine, the chlor-amyl thus formed will turn it to the right $(\alpha\,\mathrm{D} = +1{\cdot}24)$; if by bromine, it will be turned a little more $(\alpha\,\mathrm{D} = +3{\cdot}5)$; and if by iodine, still more $(\alpha\,\mathrm{D} = +5{\cdot}41)$. This is in full analogy to the behaviour of tartaric acid, as explained above, and therefrom we conclude that these substitutions take place in the wings of the asymmetrical carbon. Further, we know, as just stated, that a screw can only be formed from the horizontal rows of carbon-atoms of the above structures, because the asymmetrical carbons have not carbon-atoms on both sides in the perpendicular rows. Now the first structure, fig. 1588 G, is the only one in which hydroxyl is placed in one of the wings; consequently that must represent the correct arrangement of the various groups round the asymmetrical carbon; possibly the other amyl-alcohols also exist, but their optical behaviour must differ from the above.

I have stated above that the idea of a screw-formation as the cause of the optical properties of a large number of organic compounds is not at all a new one, but the idea has not been developed into a theory sufficiently simple and natural to be acceptable to the majority of chemists, and has, therefore, so far as I am aware, remained, like the asymmetrical carbon, a mere postulate.

The simpleness of the theory here submitted ought to be its commendation; at the same time this very simpleness and the fact that such an idea should not have presented itself to somebody else long ago make me hesitate and feel diffident in advancing it here; I must, therefore, invite the reader to accept it *cum grano salis*, like all other theories that have not stood the crucial test, which, for various reasons, I must leave to the care of greater capacities, if they think it worth their while.

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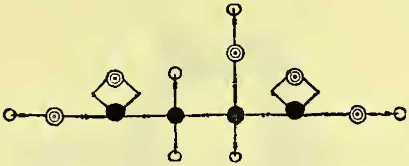
If the single bond of an asymmetrical carbon-atom changes into a double bond, the compound becomes inactive because the carbon-atom has lost its freedom to rotate round the common axis as described before, and screw-formation is made impossible, still two isomers are possible; but with the system of symbols we have been using their differences cannot find ready expression. Malic acid is the best known example of this.

The pictorial form we have given to malic acid (fig. 727, p. 186) was

Fig. 1589

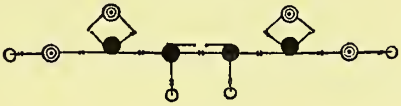


Malic acid

Its two active and one inactive stereo-isomers are explicable exactly in the same way as were those of lactic acid, and need therefore not be repeated.

When the hydroxyl and its neighbouring hydrogen are removed in the form of water, the remaining free valencies will form a double bond:

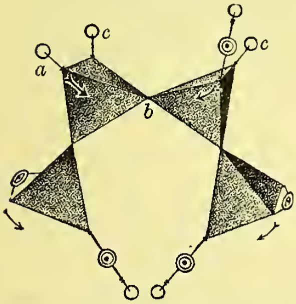
Fig. 1590



This figure represents two isomeric compounds: maleïc acid and fumaric acid. Now we will see how their differences can be explained by the tetrahedron system.

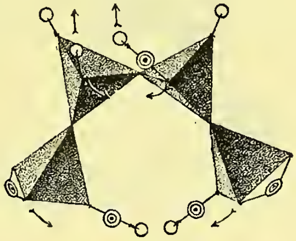
The conversion of malic acid into maleïc acid may be illustrated thus:

Fig. 1591



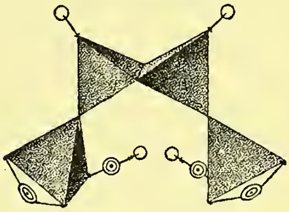
Malic acid

Fig. 1592



Double bond in course of formation

Fig. 1593

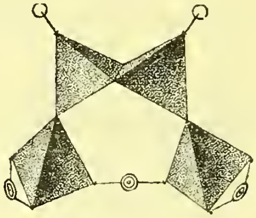


Maleïc acid

As regards the positions of the carboxyl-hydroxyls the remarks made on p. 465 hold good here also.

The carboxylic hydroxyls in this structure of maleïc acid will be seen to be in close proximity. Maleïc acid will therefore easily form an anhydride by dropping a molecule of water formed from the two hydroxyls when they come opposite each other (represented in the above figure), as they will do when the oscillations of the carbon-atoms are sufficiently increased by the application of heat.

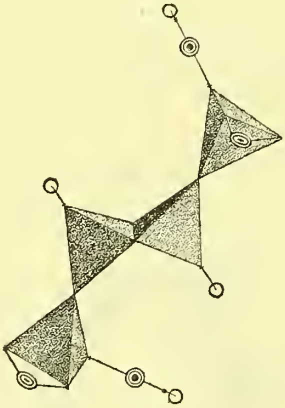
Fig. 1594



Maleïc anhydride

The arrangement of the carboxyls in maleïc acid is, however, not the only one possible; one of them may exchange places with the hydrogen-atom on its neighbouring carbon-atom, and the carboxyls, instead of being in close proximity to one another, will then be as far distant as possible. This arrangement, supposed to be present in fumaric acid, is, however, not accomplished by any jumping about of the hydrogen-atom and carboxyl-group, but effected simply by the group to the right in malic acid (fig. 1591) being carried by oscillations, increased by heat, beyond the position represented in fig. 1596, then the alcoholic hydroxyl will come sufficiently near the rear hydrogen-atom in the left-hand group (fig. 1596) to form water and create a double bond between the two central carbon-atoms corresponding to the formation of the double bond in maleïc acid (figs. 1591–1593). The following figure illustrates this arrangement:

Fig. 1595



Fumaric acid

Here, evidently, there is no chance for the hydroxyls to form water, and in fact fumaric acid does not form a fumaric anhydride, but is when heated to 200° converted into maleïc anhydride. When the double bond is broken and formed into a single bond by introduction of hydroxyl and hydrogen, both acids are reconverted into malic acid: these are all facts that find their ready explanation in the figures.

It may be asked if malic acid cannot be arranged in a similar way by having one of its carboxyls removed from its proximity to the other carboxyl and placed upon one of the two vertices of the carbon-atom occupied by hydrogen and hydroxyl, thus forming two more isomers, consequently four altogether, or five including the inactive modification, composed of equal numbers of molecules of the two active compounds. Such isomers are not known, and cannot according to our theory exist, because the carbon-atoms would at once revert to their old position on account of the carbon-atoms 1 and 2 being connected by a single bond, and their consequent movability round their common axis ($a:b$) in the following figure:

Fig. 1596

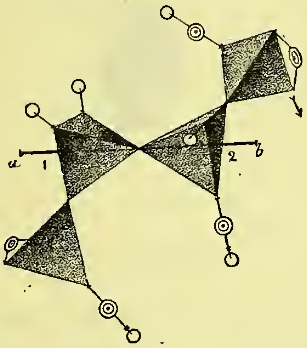
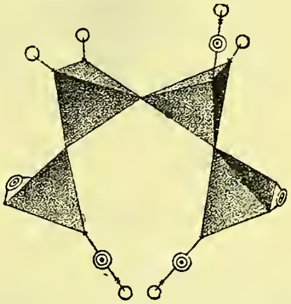


Fig. 1597



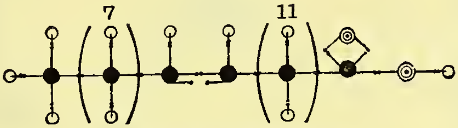
The alcoholic hydroxyl in the group 2 is in fig. 1597, facing a hydrogen in the group 1, but not in fig. 1596; consequently the former is a more favoured arrangement into which the latter will revert by a turn round the axis $a:b$, unless the oscillations through heat become sufficiently increased for the formation of fumaric acid.

Fumaric acid may be converted into maleïc acid, and *vice versâ*, by different degrees of heat, thus confirming the correctness of the theory. Another experiment has been successfully carried out on the basis of this very theory, furnishing a brilliant confirmation of its truth so far; I refer to the conversion of members of the oleïc acid-series into their respective isomers of elaïdic acid (*Ber.* xxiv. p. 4120).

Erucic acid is such a compound, which being an oily liquid is turned into the crystalline isomer brassidic acid (*vide* fig. 753, p. 193) through nitrous acid.

We have given the two acids the same structure because their differences are not conveniently expressible in our symbolic language:

Fig. 1598

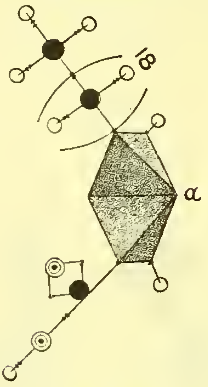


Erucic and brassidic acids

As the process entirely concerns the doubly linked carbon-atoms, these two only will be represented as tetrahedrons, retaining for the rest of the chain on all the other sides the geometrical symbols with which we now, I hope, are sufficiently familiar; by limiting the stereometrical representations to the two actually performing carbon-atoms, the process will be more intelligible; for the same reason the double bond will be placed next to the carboxyl-link.

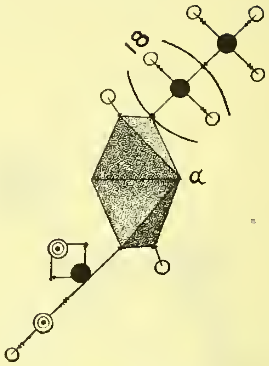
Thus represented the two acids will look like these two illustrations:

Fig. 1599



Erucic acid

Fig. 1600



Brassidic acid

The difference of structure will be seen to be this, that the upper carbon-atom has reversed its position as regards the lower one. This reversion has been effected in the following way:

First the double bond has been broken at *a*.

Compounds with double bond in an open chain easily take up by addition two suitable atoms, breaking the double bond, as frequently demonstrated on the preceding pages. Hitherto we have represented this process as being performed by two hydrogen-atoms, but it may be effected just as well, or even easier, by halogen-atoms, *e.g.* chlorine.

If we then apply chlorine to erucic acid, two such chlorine-atoms will take possession of the two valencies joined by *a*, which consequently will separate and the two carbon-atoms will assume the structure of single linkage. The process in progress and the finished position will be understood from the following illustrations:

Fig. 1601

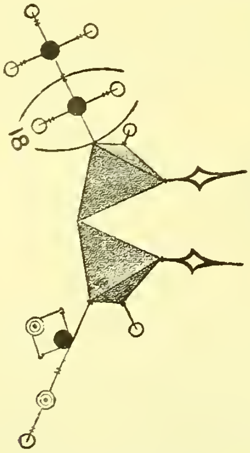
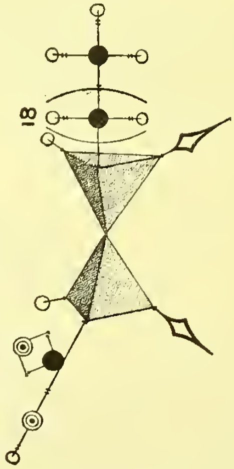
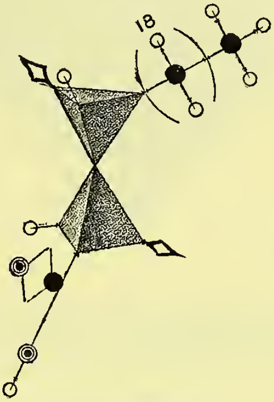


Fig. 1602



By the addition of the two chlorine-atoms, breaking the double bond of erucic acid, the first step has been made to convert it into the chlorine-compound of the corresponding fundamental acid, behenic acid (fig 755, p. 193). It will be noticed that the two chlorine-atoms are in the most proximate positions to be found in the system, two opposite vertices, a position in which there is little stability, and as a consequence the two carbon-atoms try to arrange themselves in a more stable position. That is in this case easily effected in the same way as we have seen it done in a similar case (figs. 1567 and 1568, p. 460). One of the carbon-atoms makes a turn of 120° round their common axis into the most favoured position, whereby one of the chlorine-atoms comes opposite a hydrogen, and the other faces the hydrocarbon body of the acid. We shall let the upper carbon make the movement and the result will be

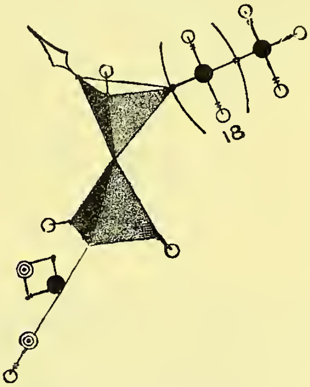
Fig. 1603



Di-chloro-behenic acid

We can first, through reducing agents, withdraw the chlorine-atom opposite the hydrocarbon and substitute it by a hydrogen-atom, converting the compound into mono-chloro-behenic acid:

Fig. 1604

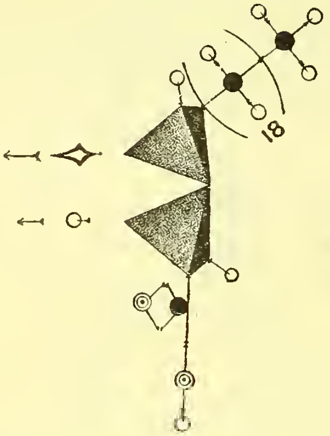


Mono-chloro-behenic acid

When finally the chlorine and its opposite hydrogen are withdrawn in the form of hydrochloric acid, by an alkali, the two free valencies thereby created close up, forming a double bond between the two carbon-atoms.

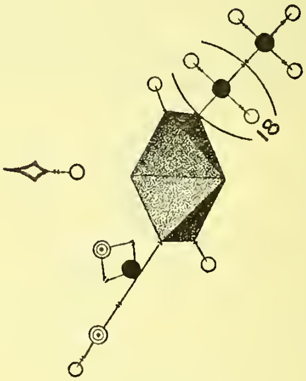
In order to make this result perfectly understood, the intermediate phase in the process is also here illustrated:

Fig. 1605



Formation of the double bond

Fig. 1606



Brassidic acid

We have thus arrived at brassidic acid from erucic acid. In the same way are to be explained, also, all the stereo-isomerisms mentioned before, *e.g.* crotonic and iso-crotonic acids, angelic and tiglic acids, &c.

---

It may perhaps be opportune, now, to examine how far the system of symbols we have chosen to represent the atomic linkage agree with these later theories.

When we again look at the carbon-atom with its four valencies, as illustrated p. 453, we can by turning it a little to the right, and making it stoop a little from the plane of the paper, give it a form similar to the one we have used all through the treatise:

Fig. 1607

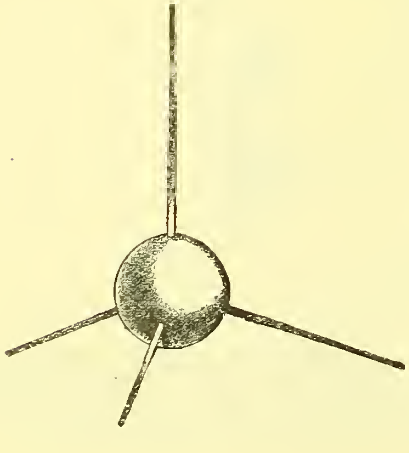
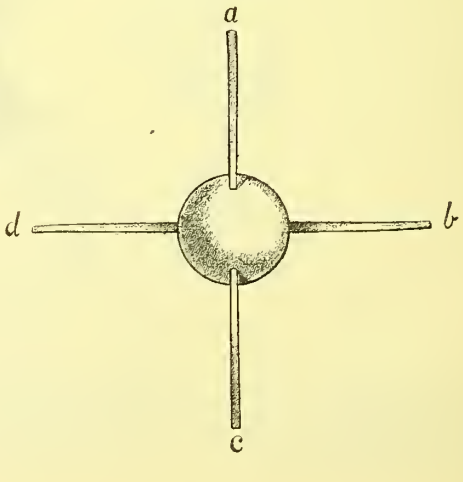
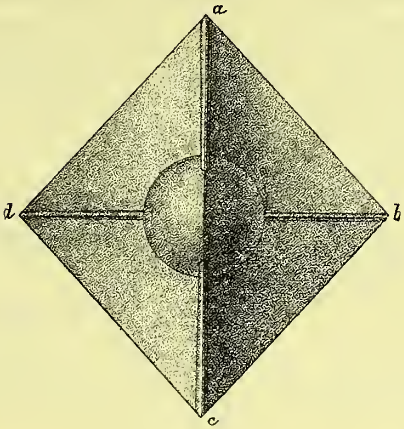


Fig. 1607 A



The configuration of the tetrahedron formed by connecting the ends of the valencies would be

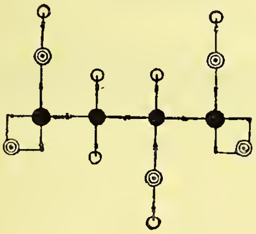
Fig. 1608



As regards single bonds, our symbols would therefore appear correct enough, provided we refrained from representing an open chain in its natural form of a not closed ring.

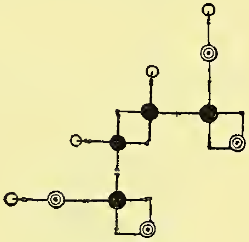
Not quite so correct is our representation of the double bond. In order to be nearer the truth, as far as we know, the valency *c* should remain in position, and not bend towards the other carbon-atom, and the connection should take place along the line *c b*. Thus the three acids, malic, maleïc, and fumaric, represented as truly as possible when drawn as a projection on a plane, would be

Fig. 1609



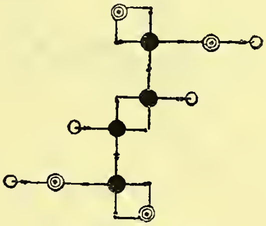
Malic acid

Fig. 1610



Maleïc acid

Fig. 1611



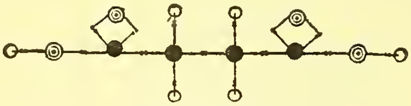
Fumaric acid

It is obvious how bewildering such a true representation would be, especially in more complex compounds with several double bonds; the two advantages which it should possess, its closer proximity to truth, and hence its capability of showing the stereo-isomerism, are as nothing to the absence, contingent thereupon, of uniformity, intelligibility, and aptitude to impress the memory; moreover, triple bonds, anyhow, could not be depicted without having recourse to perspectivity.

It would be an improvement to let the double bond form two parallel lines instead of a square, and stretch the legs of the carboxyl into the straight line; but even then the uniformity and consequent comparability with other structures would be greatly impaired. I will show this by samples thus constructed and compared with the system adopted in this treatise:

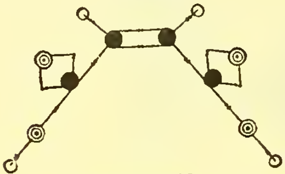
Stereometric Structures represented geometrically

Fig. 1612



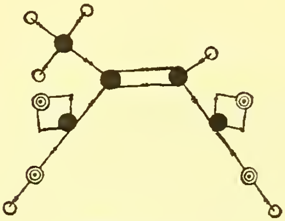
Succinic acid

Fig. 1614



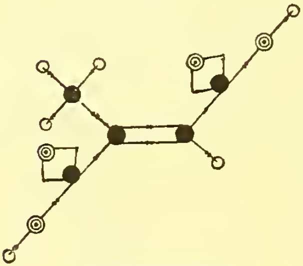
Maleïc acid

Fig. 1616



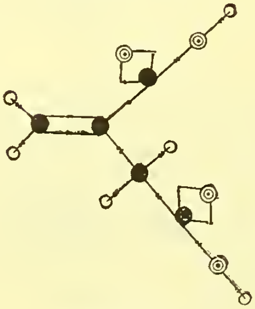
Citraconic acid

Fig. 1618



Mesaconic acid

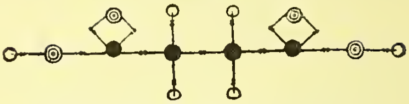
Fig. 1619



Itaconic acid

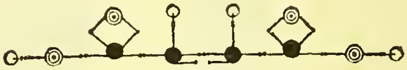
Geometric Structures

Fig. 1613



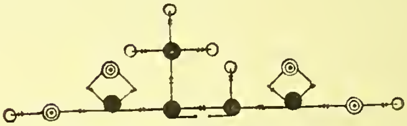
Succinic acid (*vide* fig. 714, p. 185)

Fig. 1615



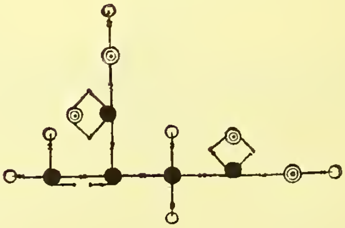
Maleïc acid (*vide* fig. 762, p. 195)

Fig. 1617



Citraconic and mesaconic acid (*vide* fig. 763, p. 195)

Fig. 1620

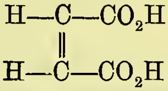


Itaconic acid (*vide* fig. 764, p. 196)

The whole difference now between the two systems is that the doubly linked carbon-atoms with all their appendices are in the stereometric structures given an upward or downward turn of 45° from the horizontal position in which they are placed in the system of this treatise. There is thus a gain to them individually, but a loss considered as a whole; the loss is, in my opinion, greater than the gain, because the derivation of one from another is not easily grasped, and they are therefore not so easily retained in memory. They are, however, generally and necessarily employed by chemists who wish to demonstrate the stereometrical differences by the instrumentality of the usual chemical letter-symbols with the minor alteration of the double bonds being placed perpendicularly. Thus the above compounds, as written in the ordinary chemical language, appear as follows:

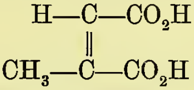
$CO_2H—(CH)_2—CO_2H$

Succinic acid



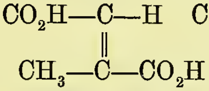
$$\begin{array}{c} H—C—CO_2H \\ \| \\ H—C—CO_2H \end{array}$$

Maleïc acid



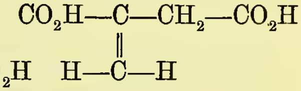
$$\begin{array}{r} H—C—CO_2H \\ \| \quad\quad \\ CH_3—C—CO_2H \end{array}$$

Citraconic acid



$$\begin{array}{l} CO_2H—C—H \\ \quad\quad\quad \| \\ \quad CH_3—C—CO_2H \end{array}$$

Mesaconic acid



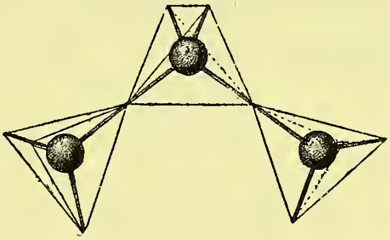
$$\begin{array}{l} CO_2H—C—CH_2—CO_2H \\ \quad\quad\quad \| \\ \quad\quad H—C—H \end{array}$$

Itaconic acid

which correspond exactly with the above.

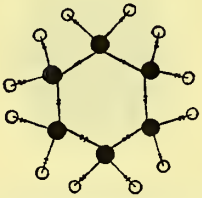
As regards the closed singly linked rings the system used has another inaccuracy, which it shares with practically all other similar representations, that is, the placing of valencies inside such ring, as the theory supposes. The illustration of part of a hexagon or pentagon will suffice to show that all valencies are outside:

Fig. 1621



A more correct representation of benzene-hexa-hydride (fig. 124, p. 26) would therefore be

Fig. 1622

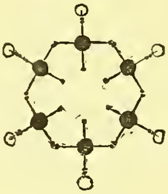


Benzene-hexa-hydrid

But the other way of representing this ring offers so many advantages, in itself and its relation to rings with double bonds, that although sometimes compelled, by want of room inside the ring, to place both valencies outside, according to the above diagram, yet preference has been given to the ring with inside valencies, in spite of its incorrectness.

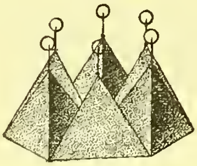
A suggestion of rather recent date places all the inside bonds of the benzene-ring in diagonal position (fig. 290, p. 55). By our system this was expressed by the following figure:

Fig. 1623



Supposing the tetrahedron-theory to be correct, there is only one mode of placing the carbons in such a way as to meet this exigency, viz. to put the tetrahedrons close together flat down on a plane:

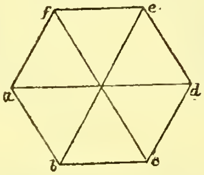
Fig. 1624



Benzene (with diagonal bonds)

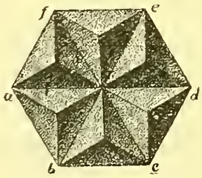
Seen from the bottom it must be represented thus:

Fig. 1625



Seen from the top the ring would therefore appear thus:

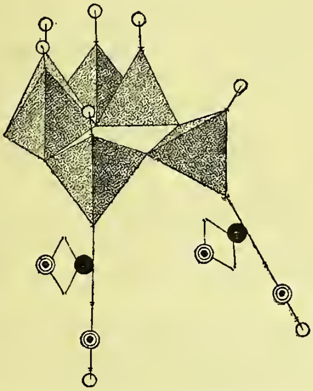
Fig. 1626



In the position represented by these figures there are evidently six double bonds, part of each affinity being spent in keeping together the six vertices in the centre. But we know they are not assumed to be at rest there; they must be supposed to vibrate round axes lying in the line of their outside edges: *a* : *b*, *b* : *c*, *c* : *d*, &c., oscillating at a tremendous rate, probably under 600 billions per second, which is the rate of the light's average vibrations, but certainly much more than 500,000 millions per second, the number of the molecule's mutual collisions in a gas. If these vibrations are not synchronal, and individually perhaps not even equally rapid, some at times slower, and others quicker, then there will be an ever-changing number and kind of bindings, varying from none to six of wholly, or partly, double or single bonds, and not only diagonal bonds, but also linkings in all sorts of cross-ways. As in all similar cases, so also in this, there must be a position that represents the mean of them all, and that may, under ordinary circumstances, be the one in which there are three double bonds and three single ones; in other words, Kekulé's formula. With circumstances altered everybody's formula may in turn be equally favoured. Thus they may all be right; a state of things I have already indicated on an earlier occasion (*vide* p. 55).

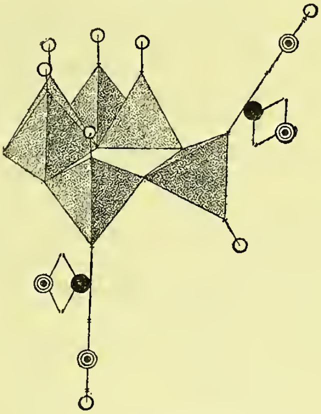
If more than six hydrogen or other atoms or groups are added to the ring, the respective tetrahedrons wheel round the said axes, $a : b$, $b : c$, $c : d$, &c., changing front until they have reached the positions indicated in fig. 1621, p. 477, the two valencies being then on the outside of the ring. When, for instance, two carboxyls are added, di-hydro-phthalic acids are obtained (comp. p. 218).

Fig. 1626 A



*Cis*-$\Delta^{3\cdot 5}$ di-hydro-phthalic acid

Fig. 1626 B

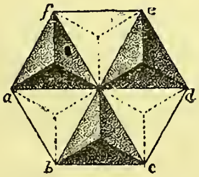


*Trans*-$\Delta^{3\cdot 5}$ di-hydro-phthalic acid

The *cis*- or maleïnoïd-form (*vide* p. 219) is also designated as *plane-symmetrical*, and the position of the carboxyls as *corresponding*; the *trans*- or fumaroïd-form as *axial-symmetrical*. The designations maleïnoïd and fumaroïd are, of course, derived from maleïc and fumaric acids, in which the carboxyls are supposed to be similarly placed; the others explain themselves.

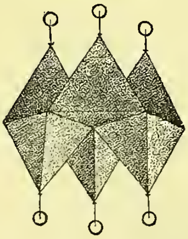
The diagonal structure was originally propounded by *Claus*, and therefore generally bears his name; it is, however, sometimes termed *Loschmidt's* or *Körner's* formula. According to *Dewar*, the carbon-atoms 1 : 4 are linked by a single bond, 2 : 3 and 5 : 6 by double bonds. An improvement upon Claus's formula is termed *Vaubel's*, in which the apices turn alternately in opposite directions, consequently thus:

Fig. 1626 c



Top view

Fig. 1626 d



Side view

The fact, however, remains that no single one of the many propounded structures meets the requirements of the benzene-ring; but any of the chemical reactions and physical properties, so far as they are known, may be explained by either one or the other.

# VALENCIES

I cannot conclude my work without referring to that which is perhaps the most perplexing character of the atoms, namely, their varying powers of combination with other atoms. We have seen carbon as a dyad and a tetrad, sulphur as a dyad, tetrad, or hexad, nitrogen and phosphorus as triads or pentads, and the former perhaps also as monad. Hydrogen we have seen as a monad under all circumstances, and likewise chlorine, although inorganic chemistry teaches us that the latter is even more changeable than any of those previously mentioned, being able to appear in no less than four different characters: monad, triad, pentad, and heptad. It is, however, remarkable that this changeable character is shown only in the presence of bodies more electro-negative than themselves. Towards more electro-positive bodies their valency is invariable, chlorine always uniting with one hydrogen-atom, sulphur with two, nitrogen with three, and carbon with four, provided that only one atom of any of the said elements enters into the combination.

Chemists have long been unwilling to attribute such a changeable property to the elements, as it somewhat disturbs our ideas of the absolutely unalterable properties of atoms, and many ingenious devices have been propounded in order to steer clear of the rock; but it has only led to such absurd consequences that they had to submit to the assumption of the apparent inconstancies of the elements in this respect.

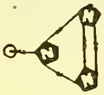
I am not aware of any existing theory propounded to explain this property, now accepted as a fact, but the discovery of hydrazoïc acid, combined with the supposition, gaining more and more ground, that the elements are not simple indivisible bodies, but compounds which we have hitherto been unable to further decompose, seems to throw more light upon this subject.

We mentioned (p. 384) that hydrazoïc acid had a close resemblance to hydrochloric acid in its chemical properties; that, in fact, the combination of the three nitrogen-atoms, like an element, played a part very similar to that of chlorine in their respective combinations with other elements or groups.

If we now accept the hypothesis of the elements being compound bodies, each atom consisting of several micro-atoms, the idea suggests itself that these micro-atoms may be tied together, like our present atoms in hydrazoïc acid, by single or double bonds. In this way the valency-variations are readily explained. Some illustrating examples will interpret the idea, if required.

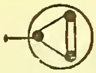
Suppose chlorine consisted of three triad micro-atoms combined like the three nitrogen-atoms in hydrazoïc acid, an atom and a molecule of chlorine and hydrochloric acid would have such structure:

Fig. 1627



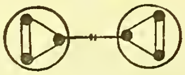
Hydrazoïc acid (*vide* fig. 1373, p. 384)

Fig. 1627 A



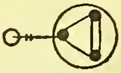
Atom of chlorine

Fig. 1628



Molecule of chlorine

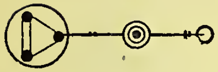
Fig. 1629



Molecule of hydrochloric acid

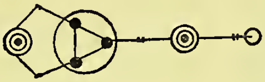
Chlorine's combinations with oxygen would be

FIG. 1630



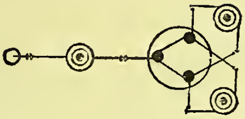
Hypochlorous acid,[1] Cl(OH)

FIG. 1631



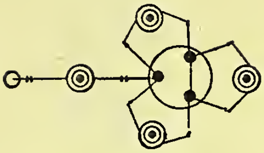
Chlorous acid,[1] ClO(OH)

FIG. 1632



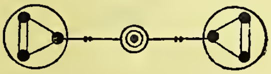
Chloric acid, $ClO_2(OH)$

FIG. 1633



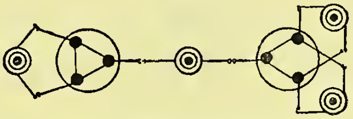
Perchloric acid, $ClO_3(OH)$

FIG. 1634



Hypochlorous anhydride, $Cl_2O$

FIG. 1635

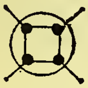


Chlorine peroxide, chlorotetroxide, $Cl_2O_4$; may be regarded as a mixed anhydride of chlorous and chloric acids

How far figs. 1632, 1633, and 1635 are probable, some of the micro-atoms being kept together only by oxygen, with no direct binding between themselves, I shall not say; by supposing seven micro-atoms in an ordinary atom, which is more likely, such direct bindings can in all cases be established. I have purposely chosen three, in order to keep up the analogy to hydrazoïc acid. It should be remembered that chlorine's combinations with oxygen are all very loose, often decomposing with an explosion into the constituent elements.

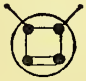
The other elements may also be supposed to consist of micro-atoms with always three valencies. Thus carbon may have four tri-valent micro-atoms:

FIG. 1636



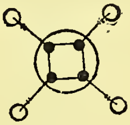
Tetra-valent carbon

FIG. 1637



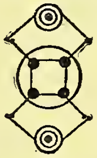
Di-valent carbon

FIG. 1638



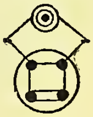
Methane

FIG. 1639



Carbon dioxide

FIG. 1640



Carbon monoxide

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[1] The constitution of the compounds mentioned on p. 271 as containing in their structures radicals of the hypothetical iodous and hypo-iodous acids has, on later and closer examination, proved very different from what it was at first supposed to be (*Ber.* xxvii. p. 502); these compounds are, now, ascertained to be substitution-products of an, as yet, hypothetical body, $HO—I—H_2$, which, analogous in its structure to hydroxyl-amine, $HO—N—H_2$ (fig. 1129, p. 318), is in chemical character more nearly related to the, also, hypothetical ammonium-hydroxide, $HO—N—H_4$ (fig. 1106, p. 312), and sulphine-hydroxide, $HO—S—H_3$ (comp. p. 286), for which reason the name of *iodonium-hydroxide*, and change of name of sulphine into *sulphonium*, have been proposed. The two hydrogen-atoms in iodonium-hydroxide may be replaced by phenyls or iodo-phenyls and the hydroxyl by iodine, *e.g.* $HO—I<\begin{matrix}(C_6H_5)\\(C_6H_5)\end{matrix}$, $HO—I<\begin{matrix}(C_6H_5)\\(C_6H_4)I\end{matrix}$, $I—I<\begin{matrix}(C_6H_5)\\(C_6H_5)\end{matrix}$, in full analogy to tetra-methyl-ammonium-hydroxide (fig. 1124, p. 316), tri-methyl-sulphine (sulphonium)-hydroxide, their chlorides and their iodides (fig. 1018, p. 286). Iodonium-hydroxide's combinations with phenyls are, like the corresponding ammonium's and sulphine's combinations with alkyls, very strong bases, closely resembling derivatives of certain metals, especially those of thallium. The structures of aristol, carvacrol-iodide, europhen, and similar compounds (p. 270) will probably have to be altered accordingly. This property of iodine as a base-forming element is new and surprising. Chlorine and bromine are probably quite ready to follow suit, and what next?

Nitrogen may have five tri-valent micro-atoms; where a compound is represented by two figures, one is intended to illustrate the structure in the free state, the other, by re-arranging the bonds, that in some of its reactions:

Fig. 1641
Mono-valent

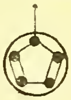


Fig. 1642
Tri-valent

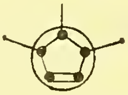


Fig. 1643
Penta-valent

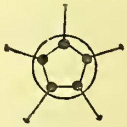
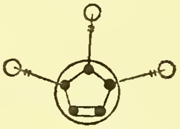
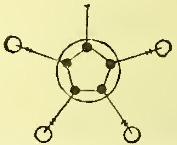


Fig. 1644



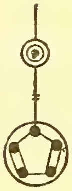
Ammonia, $NH_3$

Fig. 1645



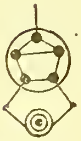
Ammonium $NH_4$ hypoth.

Fig. 1646



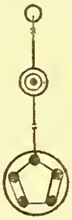
or

Fig. 1647
Tri-valent



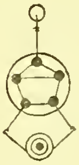
Nitric oxide, NO

Fig. 1648 A



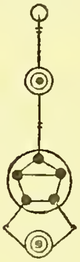
or

Fig. 1648 B



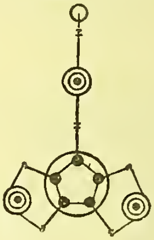
Hyponitrous acid, NOH; see also p. 301; monobasic

Fig. 1649



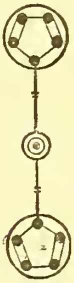
Nitrous acid, NO(OH); or $NO_2H$, *vide* p. 302; monobasic

Fig. 1650



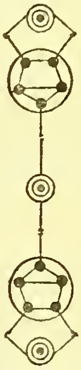
Nitric acid, $NO_2(OH)$; monobasic

Fig. 1651



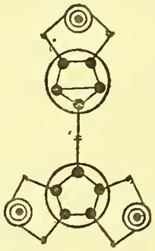
Nitrous oxide, $N_2O$; hyponitrous anhydride; is also represented as a cyclo-compound with double binding between the two nitrogen atoms, *vide* fig. 1372, p. 384.

Fig. 1652



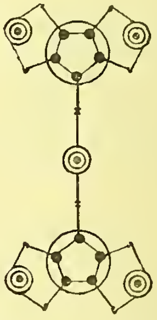
or

Fig. 1653
Tri- and penta-valent



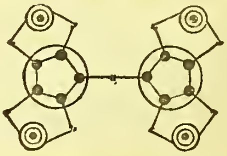
Nitrous anhydride, $N_2O_3$; the second structure is the anhydride of hyponitrous acid, fig. 1648 B, and nitric acid, explaining its composition from, and decomposition into, nitric peroxide and nitric oxide

Fig. 1654



Nitric anhydride, $N_2O_5$

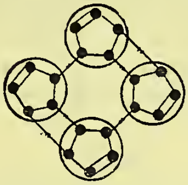
Fig. 1655



Nitric peroxide, $N_2O_4$

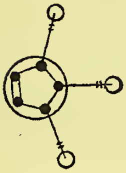
Phosphorus atomic value is analogous to that of nitrogen, and may therefore be assumed also to contain five micro-atoms. A mono-valent phosphorus is, however, unknown :

Fig. 1656



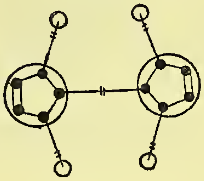
A molecule of phosphorus in the gaseous state, $P_4$

Fig. 1657



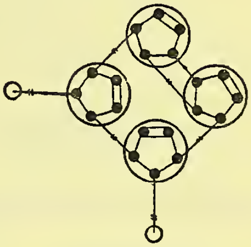
Gaseous phosphoretted hydrogen (phosphine), $PH_3$

Fig. 1658



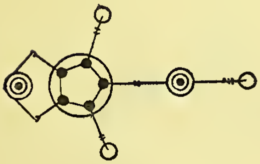
Liquid phosphoretted hydrogen, $P_2H_4$

Fig. 1659



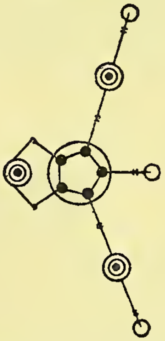
Solid phosphoretted hydrogen, $P_4H_2$

Fig. 1660



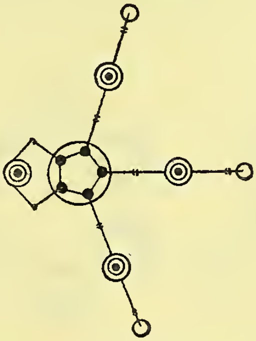
Hypophosphorous acid, $H_2PO(OH)$; monobasic

Fig. 1661



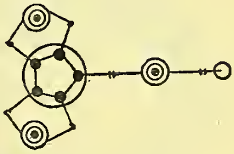
Phosphorous acid, $HPO(OH)_2$; dibasic

Fig. 1662



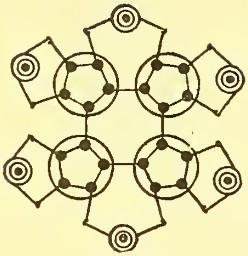
Phosphoric acid, $PO(OH)_3$; tribasic

Fig. 1663



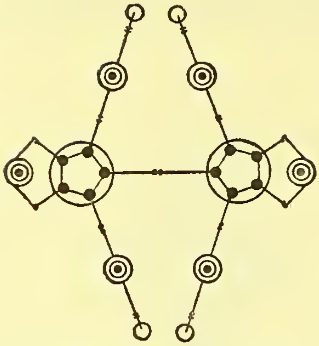
Metaphosphoric acid, $PO_2(OH)$; monobasic

Fig. 1664



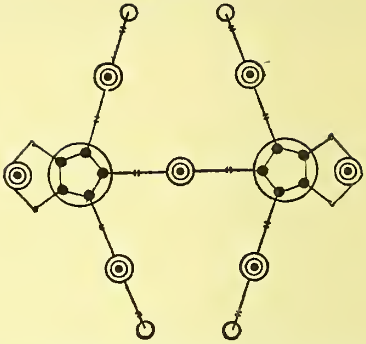
Phosphorous anhydride, $P_4O_6$; produced, as the structure shows, from four molecules of phosphorous acid by anhydride formation separating six molecules of water

Fig. 1665



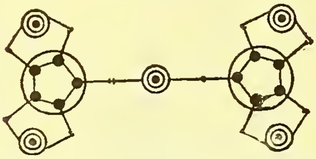
Hypophosphoric acid, $(PO(OH)_2)_2$; is a combination of phosphorous and phosphoric acid by elimination of a molecule of water (anhydride formation); tetrabasic

Fig. 1666



Pyrophosphoric acid, $(OH)_2PO\text{-}O\text{-}PO(OH)_2$; is evidently two molecules of phosphoric acid joined in anhydride fashion; tetrabasic

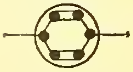
Fig. 1667



Phosphoric anhydride, $P_2O_5$; anhydride of meta-phosphoric acid consistent with its mode of preparation

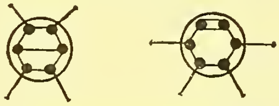
In sulphur we may assume six tri-valent micro-atoms:

Fig. 1668



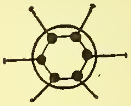
Di-valent sulphur

Fig. 1669



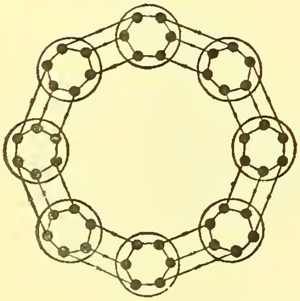
Tetra-valent sulphur

Fig. 1670



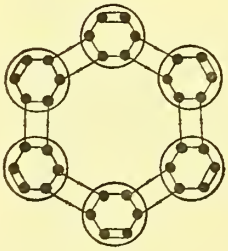
Hexa-valent sulphur

Fig. 1671



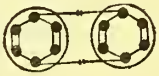
Hexa-valent atoms; a molecule of rhombic sulphur

Fig. 1672



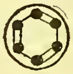
Tetra-valent atoms; a molecule of sulphur gas at 500° = $S_6$

Fig. 1673



Di-valent atoms; a molecule of sulphur gas at 1000° = $S_2$

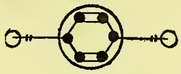
Fig. 1674



An atom of sulphur = S

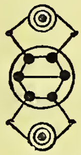
For economy of space rhombic sulphur is here represented as a molecule of eight atoms; the exact number is not known, but is probably a multiple of six. All the micro-atoms are here united by single bonds. In mono-clinic sulphur, which is formed by heating, a double bond is supposed to be formed inside each atom between two micro-atoms, easily re-arranged into single bonds, reconverting the sulphur into the rhombic modification. In sulphur-gas at 500° the molecules are split up into smaller molecules of six atoms; in the atoms are, according to the hypothesis, the same double bindings between the micro-atoms as in the mono-clinic sulphur. The sulphur-gas at 1000° is known to have a molecular combination of two atoms, in each of which the theory supposes two double bonds. Finally the atom of sulphur, which can only exist in free state at very high temperatures, has three such double bindings. The increased formation of double bonds as the temperature rises is in full accord with the tetrahedron-theory (*vide* p. 461); though the micro-atoms are not represented as tetrahedrons, still the theory must be sauce for both goose and gander.

Fig. 1675



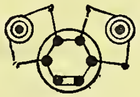
Sulphuretted hydrogen, $SH_2$

Fig. 1676



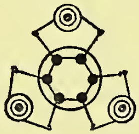
or

Fig. 1677



Sulphur dioxide (sulphuryl), also called sulphurous anhydride, $SO_2$

Fig. 1678



Sulphur trioxide, also called sulphuric anhydride, $SO_3$

Fig. 1679

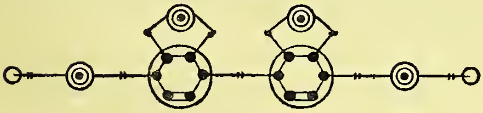
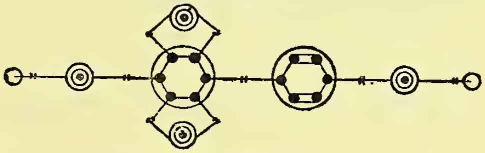


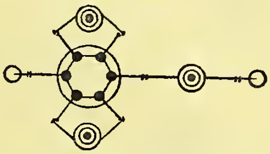
Fig. 1680



Hypo- or hydro-sulphurous acid, $OH(SO)_2OH$ or $(OH)SO_2–S–(OH)$; dibasic

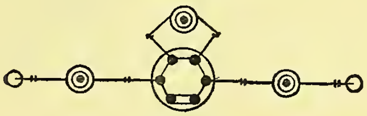
The second formula gives a ready explanation of its decomposition first into thiosulphuric acid and then into sulphur dioxide, sulphur, and water, and is therefore perhaps more correct than the first, which is, however, the one generally given.

Fig. 1681



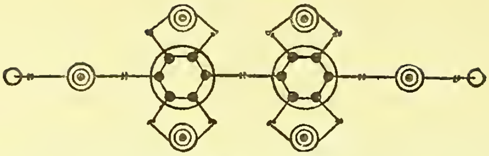
Common sulphurous acid, $HSO_2(OH)$. Both hydrogens are replaceable by bases, and the acid is therefore dibasic. This structure is a necessary consequence of the formation of sulphurous ethers from mercaptans and thio-ethers by oxidation. No acid ethers are known of the symmetrical sulphurous ethers, but both acid and neutral ethers are known from the common acid

Fig. 1682



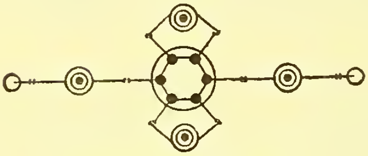
Symmetrical sulphurous acid, $SO(OH)_2$; hypoth.; dibasic

Fig. 1683



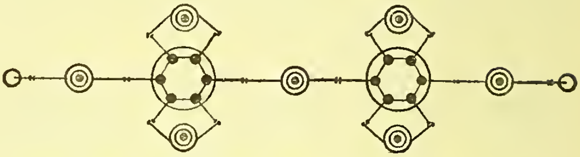
Di-thionic acid, $OH(SO_2)_2OH$ ; dibasic ; may be considered a combination of sulphuric and sulphurous acids in anhydride fashion

Fig. 1684



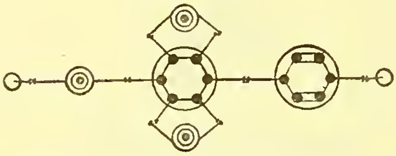
Sulphuric acid, $SO_2(OH)_2$

Fig. 1685



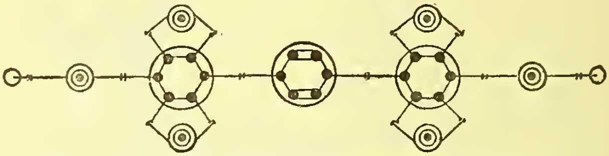
Di-sulphuric acid, $OH(SO_2)O(SO_2)OH$ ; is two molecules of sulphuric acid joined in anhydride fashion ; dibasic

Fig. 1686



Thio-sulphuric acid, $(OH)SO_2(SH)$ ; dibasic. This will be recognised as sulphuric acid in which sulphur has displaced an oxygen-atom in one of the hydroxyls

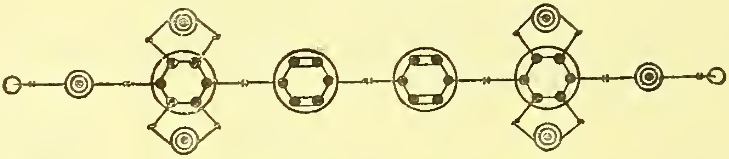
Fig. 1687



Tri-thionic acid, $OH(SO_2)S(SO_2)OH$ ; formed by the connecting oxygen in di-sulphuric acid being displaced by sulphur, or from thio-sulphuric acid and sulphuric acid, a molecule of each joining in anhydride fashion

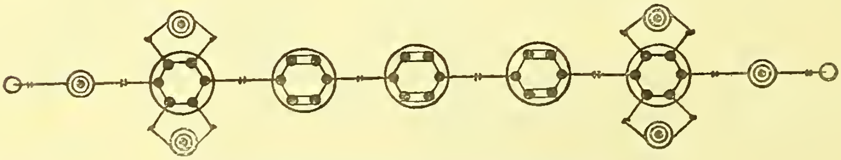
The structures of tetra- and penta-thionic acids are generally represented as a row of sulphur-atoms with a radical of sulphurous acid at each end.

Fig. 1688



Tetra-thionic acid, $S_4O_4(OH)_2$ ; dibasic

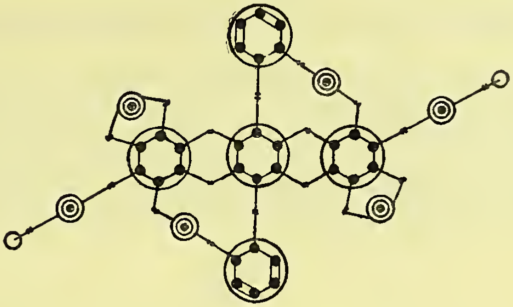
Fig. 1689



Penta-thionic acid, $S_5O_4(OH)_2$ ; dibasic

They are, however, not very likely structures, such stringing single atoms in a row of an open chain being most improbable; the structures are no doubt more complicated. There are several other ways of arranging them, but so little is known of them that the following is little more than guess-work.

Fig. 1690



It explains the decomposition of the acid into sulphurous acid, and of the penta-thionates into tri- and tetra-thionates, with separation of sulphur; its formation, however, from barium thiosulphate and chloride of sulphur is less striking than by the string structure.

So far, then, the theory works beautifully enough, and has even enabled us to see some old acquaintances in a new light; but the hypothesis has its disadvantage: it rests upon another hypothesis, not much better than a presentiment, viz. the divisibility of our present atoms, the chief support for which is the periodic law of atomic weights, their analogy now and then to homologous series, and, if you like, the theory above propounded, a sort of co-operative assurance.

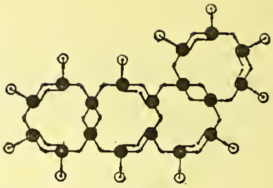
Quite the other way as regards the tetrahedron-theory. Founded on facts, it has led to discovery of new facts, and has, therefore, from a chemical point of view, reached a stage nearer truth than its precursors; yet it is not truth itself. There are still formidable difficulties to surmount, and many yet unborn theories will come and go before chemists, mathematicians, astronomers, and physicists shall agree on all points; and even then we shall still be far away from that ultimate simplicity which we shall never know—

THE TRUTH.

# ADDENDA

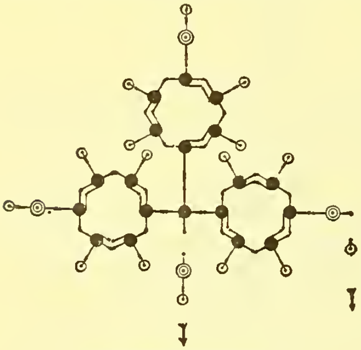
The manuscript of this treatise was finished in February 1893, but since it left my hands I have tried to keep it up to date by taking advantage of every opportunity offered during the progress of printing. A few corrections occasioned by investigations which did not come under my notice until too late must, consequently, find their place here.

Page 31.—*Chrysene* is said (*Ber.* xxvii. p. 952) to have probably this structure:

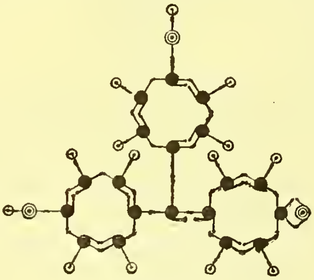


Chrysene

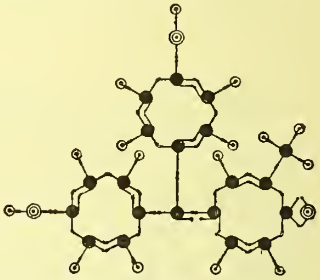
Page 108.—*Aurin* and *rosolic acid* have been found to behave in some respects like quinone, for which reason their structures and formations from tri-phenol-carbinol have been represented in a way somewhat different from that found on p. 108 (the methyl-group in fig. 468, according to Krafft, is placed on a wrong phenyl); in *Ber.* xxvi. pp. 172 and 2221 (see also *Nietzki, Chemie d. org. Farbstoffe*, $2^{te}$ Aufl. p. 88) the following explanation is given by which the elimination of a molecule of water causes a rearrangement of the bonds only, but no intramolecular jumping about of groups:



Tri-phenol-carbinol

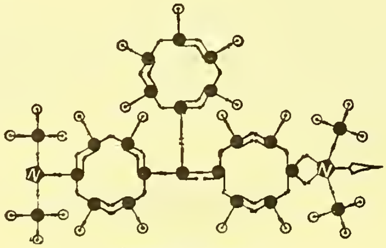


Aurin

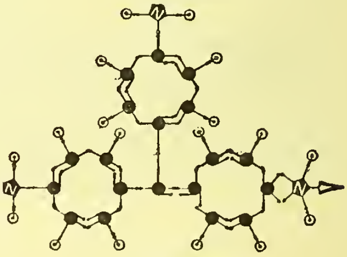


Rosolic acid

As a consequence, *malachite-green* (fig. 1279, p. 361) and *para-fuchsine* (fig. 1284, p. 362) must have such structures:

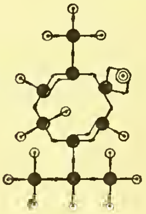


Malachite-green

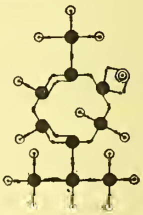


Para-fuchsine

Page 143.—*Carvol.* According to *Ber.* xxvii. p. 814, the structure, fig. 586, is that of *iso-carvol; carvol* and another isomer, *eucarvol*, are represented thus:

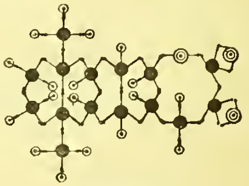


Carvol



Eucarvol

Page 226.—The latest, but probably not last, suggestion of the structure of *santonin* (*Ber.* xxvii. Ref. p. 24; *Arch. d. Ph.* ccxxxi. p. 695) is this:



Santonin

London: May 1894.

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